Influence of Water Immersion Post-Treatment Parameters on Trivalent Chromium Conversion Coatings Formed on AA2024-T351 Alloy

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In this work, the influence of water immersion post-treatment, with consideration of temperature and pH values, on trivalent chromium conversion coating morphologies, compositions and corrosion protection has been investigated, using high-resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy and electrochemical impedance spectroscopy. Compared to the coating formed without the water immersion post-treatment, the post-treatment in the deionized water bath at 40°C evidently reduced the concentrations of fluoride-containing constituents and increased the extent of oxides/hydroxides across the coating. Consequently, the enhanced corrosion protection property was investigated in the post-treated coatings during full immersion in naturally-aerated NaCl solution with mass fraction of 3.5%. In terms of water pH effects, the coatings displayed comparable thicknesses after post-treatment in the as-prepared deionized water bath (pH 5) and neutral water bath (pH 7); However, a considerable shrinkage was observed in the caustic water bath (pH 9). It was found that the resultant corrosion resistance of the coatings was greatest after post-coating treatment in the water bath of pH 5 and the least for pH 9. Inductively coupled plasma-atomic emission spectroscopy was used to trace small amounts of Zr and Cr elements in the used water baths. A robust chemical titration, adding 1, 5-diaminonaphthalene into the used water baths, revealed that Cr species were only in trivalent form.

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For AA2024 aluminum alloy, the presence of copper and magnesium elements increases the alloy susceptibility to localized corrosion. Therefore, chromate conversion coatings were used to improve the surface resistance against corrosion by a dipping process. However, the toxic hexavalent chromium species in chromate conversion coatings are an ecological concern and, hence, the chromate conversion coating process has been highly regulated by legislation such as the Restriction of Hazardous Substances (RoHS).

In this regard, trivalent chromium conversion (TCC) coatings are a promising alternative due to the low toxicity of trivalent chromium species. Such coating process on AA2024 alloy, driven by the increased pH, consists of surface activation by fluorine attack and coating initiation around second-phase particle and lateral growth on the macroscopic alloy surface. The freshly-formed coatings have many hydrated channels and the post-treatment in air for 24h can reduce the coating porosity to enhance the corrosion protection while maintaining the hydrated structure. In terms of coating structure, Zr- and Cr-rich oxides comprise the outer layer above a fluoroaluminate layer. Notably, a significant amount of fluoride constituent at the coating base was found and it correlated with the locally enhanced corrosion of aluminum substrate, which was assigned with the fluorine attack. Fluoride accumulation, especially after prolonged conversion treatment, is a composition challenge for the optimal coating process to provide sufficient corrosion resistance.

After the conversion treatment in the trivalent chromium-based solution, immediate tap-water rinsing for 120 s has been used to offer reproducible structure and performance, for reasons that currently remain unclear. Furthermore, the use of more basic tap water (pH 6.8) was critical to stabilize the hydroxide constituents in the coating compared with ultrapure water (pH 5.8). In this sense, the post-coating treatment in a water bath to replace the water rinsing process is expected to play a similar role in stabilizing the coatings. In this regard, the stabilization mechanism was possibly related to a sealing process in reducing the coating defects, which has been revealed in an anodic film after boiled water post-treatment. In terms of the Cr(VI) species formed in the air-aged TCC coatings on AA2024 alloys, the water immersion post-treatment, by adding reducing agents, is a promising process in providing an eco-friendly solution. In this sense, understanding the influencing parameters of the water bath post-treatment on the corrosion protection performance is of great importance for an eco-friendly coating process.

In the present study, high-resolution transmission electron microscopy, associated with energy-dispersive X-ray spectroscopy, and electrochemical impedance spectroscopy have been used to investigate the effects of temperature and pH values of the deionized water bath on the coating morphology, composition and corrosion protection performance.

Experimental

Specimens and preparations.—AA2024-T351 alloy (supplied by Airbus, U.K.) specimens with dimensions of 30 × 24 mm were first cleaned with acetone, ethanol and deionized water, and then mechanically polished from 400 up to a 4000 grit finish. The etching and desmutting pre-treatments proceeds as follows: (i) etching in NaOH solution of mass fraction 5% at 60°C for 60 s and (ii) desmutting in HNO3 solution of volume fraction 50% at room temperature for 30 s. All the pre-treatments were followed rinsing with deionized water and drying in a cool-air stream.

After such pre-treatments, the alloy specimens were coated in SurTec 650 chromiAl bath (SurTec Corp) at pH 3.9 and 40°C for 120, 300 and 600 s, followed by immersion in the deionized water bath (~200 ml) for 120 s. For the parameters of the deionized water bath, the temperature ranged from 20°C (cold water) to 40°C (warm water). The pH value of as-received deionized water at 40°C was approximately 5 and the pH levels of 7 and 9 of the warm water bath were created by addition of NaOH droplets with mass fraction of 1%. Subsequently, the specimens were rinsed by deionized water, dried in a cool-air stream and left in the laboratory for 24h before the experimental tests. The specimen codes for the coatings without water immersion treatment, immersion in the cold water and immersion in the warm water are I, II and III, respectively.

In order to investigate the chemistry of Cr species, the titration methodology was used as detailed by Rochester et al. Compared to the Cr(III) species, the Cr(VI) species (1, 5-DPL) is highly sensitive to the presence of Cr(VI) species to generate the violet-purple complex, being a robust titration test for Cr(VI). In the present study, the solution of 5 g / 1, 5-DPL (97%,...
Sigma-Aldrich (UK), 50 ml deionized water and 50 ml acetone was prepared and then used in the droplet titration test for Cr(VI) species.15

Specimen characterization.—The electron transparent cross sections (∼30 nm thick) of TCC coated alloy were prepared using the LEICA EM UC6 ultramicrotome, with a diamond knife.16 Transmission electron microscopy (TEM) was used to examine the morphologies and thicknesses of the ultramicrotomed slices employing a JEOL 2000FX II with an accelerating voltage of 120 kV. The high-resolution FEI Titan G2 80-200 ChemiSTEM, equipped with four energy dispersive X-ray spectroscopy (EDS) detectors, was also used to investigate the elemental contents of the specimens, operated at 200 kV. Furthermore, the TEM/EDS mapping data were analyzed with the Microanalysis Software (Bruker, UK). In addition, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), using the PerkinElmer Optima 5300 dual view instrument, was used to trace whether or not Zr and Cr elements were present in the used water bath in the post-coating treatments. To check the reproducibility, two individual samples at the same condition were analyzed.

Electrochemical measurements.—All electrochemical measurements used a three-electrode cell system, consisting of a saturated calomel electrode (reference electrode, \( E^0 = 0.241 \text{ V vs. SHE} \)), a platinum wire counter electrode and a working electrode with an exposed area of ∼2.25 cm².

The Solarton electrochemical workstation instrument was used with a Modulab software controller to measure the electrochemical behavior of the TCC coated alloys in naturally-aerated NaCl solution of mass fraction 3.5%. The electrochemical measurement process includes (i) open circuit potential (OCP) measurements for 30 min to stabilize the coating surface condition and (ii) electrochemical impedance spectroscopy (EIS) from \( 5 \times 10^2 \text{ to } 10^{-2} \text{ Hz} \), applying a sinusoidal potential waveform with 10 mV amplitudes about the OCP level. All data were processed by the ZView software according to the equivalent circuit model.17 In order to provide good reproducibility, electrochemical measurements in the same conditions were repeated three times.

Results and Discussion

Coating morphology.—Bright field transmission electron micrographs of ultramicrotomed cross-sections of trivalent chromium conversion coatings formed for 120 s with and without water immersion treatment are shown in Figure 1. For specimen I without water immersion post-treatment (Figure 1a), detachment at the coating base was observed. Such detachment may be attributed to either ultramicrotomy sample preparation16 or shrinkage of the film in vacuum.1 In terms of specimen II (Figure 1b), the locally enhanced corrosion was evident at the coating base, which is attributed to the fluorine enrichment.6 The coatings formed without water immersion post-treatment and with the cold water immersion treatment displayed similar morphologies to the previous report that used the different commercial trivalent chromium bath.4,9 By contrast, specimen III (Figure 1c) revealed intact cross sections and detachment at the coating base was undetectable, indicating the stabilization effect by water immersion at 40 °C. Furthermore, the overall thickness of TCC coatings formed on matrix (Figure 1) is presented in Figure 2, where the statistical data were obtained from six measurements of six individual slices.6 Consequently, the thicknesses revealed ∼37 ± 1.67, 39 ± 0.76 and 40 ± 0.62 nm for the specimens after I, II and III treatments, respectively. Thus, the post-coating treatment in a water bath, especially at 40 °C, can generate a thicker and intact cross section.

In terms of the water temperature effects on the coating formed for 300 s, the cross-sectional morphologies and thickness plots are shown in Figures 3 and 4, respectively. TCC coatings after post-treatments I and II (Figures 3a and 3b) displayed defects at the coating base and, interestingly, the warm water treatment (Figure 3c) revealed a uniform cross section with a thicker alumina layer along the substrate. Furthermore, the coating thickness after treatment III revealed the
maximum values of $47 \pm 1.44$ nm (Figure 4), consistent with the improved morphologies of the coating formed for 120 s by water treatment III. The stabilization role of water immersion at 40°C is assigned to the improved coating composition as discussed in the following analyses.

The trivalent chromium conversion coating displays a hydrated nature and the formation process is driven by the increased pH environment, attributed to the cathodic reactions during conversion treatment.8,18 In this sense, the pH level of a deionized water bath in the post-coating treatment is one key parameter in influencing coating morphologies. Figures 5a–5d show the transmission electron micrographs and thickness plots of the TCC coatings formed for 300 s with dependence on the pH values of the warm water bath (40°C). Regarding the cross-sectional morphologies, all specimens (Figures 5a–5c) displayed a similar feature of an intact outer layer over an alumina layer. Notably, the coating after a caustic water immersion (pH 9, Figure 5c) displayed a significant shrinkage. Figure 5d summarizes the pH-dependent thicknesses of ~44, 44 and 34 nm after water immersion at pH 5, 7 and 9 respectively. Compared to the coating after post-coating treatment in the as-prepared warm water bath (pH 5), the caustic water bath (pH 9) led to a ~30% decrease in thickness of the freshly-formed coating. As a consequence, the latter specimens with reduced coating thickness possibly reduced corrosion resistance as revealed in the following electrochemical tests.

Coating composition.—For the post-treatment in the water bath (pH 5, 40°C), high-resolution TEM/EDS mapping analyses were used to investigate the elemental profiles across the coatings and Figure 6l shows an example of the coatings formed for 300 s, followed by the warm water post-treatment. Evidently, the two-layer coating structure displayed the same composition as the previous report, consisting of a Zr-/Cr-rich outer layer over the fluoroaluminate inner layer.6 Notably, the fluorine profile revealed the enrichment at the coating base, indicating the limited effect by warm water immersion post-treatment. In terms of the elemental quantification of coating cross sections, the present work focused on the outer and main coating material (outlined in Figure 6). Correspondingly, the elemental concentrations by weight in the analysis area are presented in Table I.

In Table I, Zr, Cr, O and F are the main constituents of the coatings formed for 300 s after post-treatments I, II and III, where the carbon contamination resulted from the deionized water.6 Compared to the coating without the post-coating treatment in the water bath (post-treatment I, Table I), the coatings after post-treatments II and III displayed an evident decrease in the amount of Zr and Cr constituents. Such a finding may result from the egress of surface contaminations of electrolyte anions into the deionized water bath as discussed above. In addition, the lower temperature of post-treatment II possibly encouraged Zr and Cr anions away from the film-electrolyte interface. Therefore, the resultant coatings after post-treatment II show the lowest Zr and Cr amounts, which is also consistent with the later ICP-AES analysis of the used water (Table V). The chemistry of the coating surface with dependence on the temperature of water bath will be discussed in our next paper using X-ray photoelectron spectroscopy (XPS).
A mass fraction of $\sim 5\%$ fluorine was measured in the coating without the water immersion post-treatment. Furthermore, the atomic ratios of fluorine relative to the combined metals of Al, Zr and Cr were 0.04, 0.05 and 0.15 for the specimens after treatments III, II and I, respectively. It revealed a significant decrease of fluorine-rich components after the water immersion treatment, especially for the 40°C condition, attributed to the enhanced diffusion kinetics of free fluorine ions away from the coating region. In addition to the improved fluorine content, the oxygen mass fractions of 40 and 30% were measured in the coatings after treatments III and I, respectively, and the corresponding atomic ratios of oxygen with respect to the combined metals were 3.4 and 2.4, respectively. For the surface chemistry of anodic film, Alexander et al. used the variable-angle XPS and medium-energy ion scattering (MEIS) to reveal a hydroxyl-rich surface region of thickness that varied linearly with the total oxide thickness. The formation of a hydroxyl-rich outermost layer was associated with the presence of fluorine enrichment at the coating base. For the coating after water treatment, consistent with the literature.

Electrochemical behavior.—The influencing parameters of the water bath immersion post-treatment on the corrosion protection, provided by the TCC coatings, were investigated by electrochemical impedance spectroscopy (EIS) in naturally-aerated NaCl solution of mass fraction 3.5%. The equivalent circuit models in Figure 7 were used to interpret the impedance responses and the fitting results are shown in Tables II, III and IV. The impedance modulus- and phase angle-frequency plots in Figures 8, 9 and 10 display the electrochemical behavior of the coatings with dependence on water temperature and pH variance. The open-circuit potentials prior to the EIS scans were all around $-600$ mV_SCE, consistent with the literature. Notably, the low-frequency inductive part emerged as evidenced by the positive phase angles for bare alloy during full immersion in NaCl solution of mass fraction 3.5% (indicated by the arrow, Figure 8b). It pertained to the chloride ion effects, for example, either a diffusion process within a chloride layer on the surface of bare alloy or the faradic process of the localized corrosion.

In terms of specimens II (Table II), the charge-transfer resistance, $R_p$, revealed an increased magnitude of $\sim 15$ times in the coating formed for 300 s compared to that of the bare alloy ($\sim 3.3 \times 10^7$ $\Omega$ cm$^2$). By contrast, a small decrease of charge-transfer resistance was evident in the coating formed for 600 s, which could be attributed to the presence of fluorine enrichment at the coating base. For the coating resistances ($R_{coat}$), the increased values from 45 $\Omega$ cm$^2$ (120 s) up to 153 $\Omega$ cm$^2$ (600 s) were associated with thickening of the coating with prolonged conversion treatment. For the capacitance property, Figure 9b shows one time constant around $\sim 10^4$ Hz for the bare alloys, while two visible time constants ($\sim 10^3$ and $10^4$ Hz) were presented for the coated specimens. The constant phase elements (CPEs) were used to represent the non-ideal capacitance because their phase angles were less than 90°. In terms of the coating region ($Q_{coat}$ and $n_{coat}$), the higher value of $Q_{coat}$ ($1.2 \times 10^{-5}$ $s^2/(\Omega$ cm$^2$)) and lower homogeneity ratio of $n_{coat}$ (0.81) in the coating formed for 120 s revealed the most heterogeneous coating on the alloy surface. It is associated with the influence of protruded particles on the coating deposition process, and the prolonged conversion treatment improved the coating homogeneity on the particles and the matrix as evidenced by the improved capacitances of coated region. For the coating/substrate interface ($Q_{dl}$ and $n_{dl}$), the coated specimens show decreased values of $Q_{dl}$, indicating improved capacitance properties. This was assigned to the relatively thicker alumina layer after the prolonged conversion treatment, consistent with the general positive shift of the OCP evolution during immersion in the trivalent chromium bath.

Table III shows the equivalent circuit values of TCC coatings after treatment III (40°C), where the alloys after conversion treatment for 600 s displayed the best corrosion protection. The resistances of the coating region ($R_{coat}$) revealed a smaller extent of improvement than
Figure 6. TEM/EDS mapping of the coatings formed for 300 s, followed by the post-treatment in the water bath (pH 5, 40°C), where the outlined red square represented the outer layer for the elemental analyses in Table I.

Figure 7. Equivalent circuit model of (a) $R(QR)$ for the bare alloy and (b) $R(Q(R(QR)))$ for the coating system on the alloys, where $R_e$, $R_{coat}$ and $R_p$ represented the electrolyte resistance, the resistance of coating defects or channels and the charge-transfer resistance respectively. The time constant elements were represented by CPE symbols.

Table I. TEM/EDS analyses of elemental concentration by weight in the outer coating layer, where the coating was prepared in the trivalent chromium bath for 300 s, followed by immersion post-treatment in a warm water bath (40°C, pH 5).

| Specimen | Weight % | C      | O      | F      | S      | Al     | Cu     | Zr     | Cr     |
|----------|----------|--------|--------|--------|--------|--------|--------|--------|--------|
| I        | 3.8 ± 0.6| 30.9 ± 0.7| 2.3 ± 0.2| 0.7 ± 0.1| 3.0 ± 0.2| 1.1 ± 0.1| 50.5 ± 0.3| 7.7 ± 0.2|
| II       | 31.2 ± 7.4| 35.0 ± 4.5| 0.5 ± 0.1| 0.6 ± 0.1| 4.4 ± 0.6| 0.2 ± 0.1| 24.8 ± 2.6| 3.0 ± 0.9|
| III      | 15.8 ± 3.8| 37.3 ± 1.5| 0.3 ± 0.1| 0.6 ± 0.1| 4.5 ± 0.4| 0.5 ± 0.1| 37.0 ± 1.9| 4.1 ± 0.3|

The influence of the pH value of the warm water bath (40°C) on the corrosion protection of TCC coatings formed for 600 s was also investigated, as shown in Figure 10 with the fitting results presented in Table IV. With increasing pH value from 5, 7 to 9, the resistances of the coating defects ($R_{coat}$) and the charge-transfer resistance ($R_p$) decreased, possibly attributed to the condensation effect of the basic solution on the hydrated coatings. Interestingly, the capacitance values of $Q_{dl}$ were reduced from $\sim 4.4 \times 10^{-6}$ to $2.1 \times 10^{-5} \text{s}^2/(\Omega \text{cm}^2)$, which means that the inner layer became more intact and stable to maintain the larger capacitance property. By contrast, the outer layer displayed a considerable deterioration as evidenced by the increased value of $Q_{coat}$ from $\sim 7.4 \times 10^{-6}$ to $14.3 \times 10^{-5} \text{s}^2/(\Omega \text{cm}^2)$.

In summary, the higher atomic ratios of oxygen in the coating layer with respect to the combined metal components produced more hydrated coatings after post-treatment in the warm water bath.
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Table II. Parameters of the TCC coatings/alloy systems obtained on the base of the equivalent circuits, where the coatings were post-treated in the cold water bath (20°C, 120 s). The bare alloys were named as '0 s'.

| t (s) | R_e, Ω cm² | R coat, Ω cm² | R_p, Ω cm² | Q_all, s^2/(Ω cm²) | n_all | Q coat, s^2/(Ω cm²) | n coat |
|------|-------------|--------------|-------------|-------------------|-------|-------------------|-------|
| 0    | 14 (±1)     | -            | 3351 (±340) | 2.8 (±0.6)E-4     | 0.92  | -                 | -     |
| 120  | 16 (±1)     | 45 (±3)      | 16325 (±390)| 7.8 (±0.6)E-6     | 0.94  | 1.2 (±0.1)E-5     | 0.81  |
| 300  | 13 (±1)     | 116 (±3)     | 53826 (±306)| 7.1 (±0.2)E-6     | 0.94  | 7.2 (±0.1)E-6     | 0.88  |
| 600  | 16 (±1)     | 153 (±2)     | 42066 (±322)| 6.4 (±0.1)E-6     | 0.94  | 8.6 (±0.1)E-6     | 0.88  |

Table III. Parameters of the TCC coatings/alloy systems obtained from the fittings of the experimental EIS data according to the equivalent circuit $R(Q(R(QR)))$, where the coatings were formed for 600 s and then immersed in the water bath (40°C, 120 s).

| t (s) | R_e, Ω cm² | R coat, Ω cm² | R_p, Ω cm² | Q_all, s^2/(Ω cm²) | n_all | Q coat, s^2/(Ω cm²) | n coat |
|------|-------------|--------------|-------------|-------------------|-------|-------------------|-------|
| 120  | 13 (±1)     | 36 (±2)      | 25321 (±315)| 6.0 (±0.2)E-6     | 0.94  | 1.2 (±0.1)E-5     | 0.87  |
| 300  | 14 (±1)     | 298 (±2)     | 33345 (±262)| 3.4 (±0.2)E-6     | 0.94  | 7.2 (±0.1)E-6     | 0.89  |
| 600  | 14 (±1)     | 212 (±3)     | 93084 (±305)| 4.4 (±0.2)E-6     | 0.98  | 7.3 (±0.1)E-6     | 0.89  |

Table IV. Parameters of the TCC coatings/alloy systems obtained from the fittings of the EIS data, where the coatings were formed for 600 s and then immersed in the water bath (40°C) for 120 s. The effect of the pH-dependent corrosion protection property was investigated.

| pH   | R_e, Ω cm² | R coat, Ω cm² | R_p, Ω cm² | Q_all, s^2/(Ω cm²) | n_all | Q coat, s^2/(Ω cm²) | n coat |
|------|-------------|--------------|-------------|-------------------|-------|-------------------|-------|
| pH 5 | 14 (±1)     | 212 (±3)     | 93084 (±305)| 4.4 (±0.2)E-6     | 0.98  | 7.4 (±0.1)E-6     | 0.89  |
| pH 7 | 13 (±1)     | 112 (±2)     | 46420 (±312)| 6.1 (±0.3)E-6     | 0.91  | 7.6 (±0.3)E-6     | 0.88  |
| pH 9 | 15 (±1)     | 101 (±2)     | 25924 (±305)| 2.1 (±0.1)E-6     | 1 (±0.1)| 1.4 (±0.4)E-6     | 0.86  |

Figure 8. (a) Impedance modulus-frequency and (b) phase angle-frequency plots for the bare and coated alloys during full immersion in naturally-aerated NaCl solution of mass fraction 3.5%, where the coatings were formed for 120, 300 and 600 s after post-treatment II.

Figure 9. (a) Impedance modulus-frequency and (b) phase angle-frequency plots for the coated alloys during full immersion in naturally-aerated NaCl solution of mass fraction 3.5%, where the coatings were formed for 120, 300 and 600 s after post-treatment II.
Furthermore, the warm water bath encouraged the free fluorine diffusion away from the coating to decrease fluorine-containing constituents and to stabilize the freshly-formed coating.\(^6\) In terms of the temperature-dependent coating thickness, it correlates with the gel-like nature of the trivalent chromium conversion coating, which shrinks sufficiently at low temperature.\(^2,6\) As a consequence, the coating after post-treatment in the warm water bath (40°C) showed a reduction of coating defects (\(R_{coat}\)) compared to the specimens after treatment II (20°C). Furthermore, the post-treatment of immersion in the warm water can also produce an improved inner coating layer, especially in the coating formed for 600 s, as evidenced by the two times increase in the charge-transfer resistances than that after cold water post-treatment.

In terms of pH effects, the hydrated TCC coating was regarded as a gel-like film with the nanosized channels being influenced by the effects of the pH variance in the water bath.\(^8\) The pH effect profile was similar to the pH-dependent silicate growth, assigned to the competition between condensation, hydration and dissolution process in the aqueous solution.\(^27,28\) Considering the negligible effect of trivalent chromium species on pH value, the same effect is expected to happen on such coated particles. Thus, the pH-dependent influence of the water bath on coating thickness was a complex function of the hydration and condensation. The post-treatment of immersion in the deionized water bath (pH 5, 40°C) provides the best barrier performance as evidenced by the 

\[\sim 10^4 \Omega \text{cm}^2\] 

charge-transfer resistances that were increased by \(\sim 30\) times compared to that of the bare alloy.

**Water bath analysis.**—As-prepared and used water baths (20 and 40°C) in post-coating treatments of the coatings after conversion treatment for 300 s were analyzed by ICP-AES. Table V shows a small amount of Zr and Cr species in both used water baths, where the cold water bath used in the post-coating treatment II produced a higher level of Zr and Cr. This behavior may result from the physical absorption of Zr and Cr anions on the fresh coating surface.\(^22\) In this regard, Skeldon et al.\(^20\) used ion beam analysis to reveal the contamination or incorporation of electrolyte anions in the surface of a barrier-type anodic film with dependence on the preferential adsorption of different anions. Similarly, Zr and Cr species in the Cr(III)-based solution were suggested to physically adsorb on the coating-solution interface, and then, the post-coating treatment in the water bath can remove the anion contaminations away from the coating-water interface into the water bath.

Concerning the presence of Cr(VI) species in freshly-formed coating on AA\(^{11}\), the possibility of Cr(VI) species in the samples present was studied using a chemical titration test.\(^12\) The I, 5-DPL-containing droplets were added into the as-prepared and used water baths (20 and 40°C) and the resultant solution displayed the absence of a violet-purple color, suggesting that Cr species in the used water baths were not in hexavalent form. This is in agreement with a previous report of the undetectable Cr(VI) species in the freshly-formed coatings on AA2024 alloys by Raman spectroscopy.\(^14\)

**Conclusions**

1. The coating after post-treatment in the deionized water at 40°C revealed a significant reduction of F-rich constituents and an increased extent of oxides/hydroxides. Therefore, the enhanced corrosion protection properties were investigated.
2. The caustic water bath (pH 9) led to a considerable coating shrinkage, deteriorating the corrosion protection property. By contrast, the as-prepared deionized water and neutral water bath can provide appreciable thickness and better corrosion resistances.
3. The coating formed for 600 s, followed by the post-treatment of immersion in the deionized water bath (40°C, pH 5) for 120 seconds revealed an optimal corrosion protection property for the AA2024-T351 alloy.
4. The I, 5-DPL-containing droplets added into the used water bath in the post-coating treatments revealed that Cr species in the water bath, egressing from the coating-water interface, were only trivalent chromium species.

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![Figure 10](image-url)  
**Figure 10.** (a) Impedance modulus-frequency and (b) phase angle-frequency plots for the coated alloys during full immersion in naturally-aerated NaCl solution of mass fraction 3.5%, where the TCC coatings were formed for 600 s after post-treatments III (40°C) with dependence on pH 5, 7 and 9.

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**Table V.** Elemental quantity (mg/l) in the as-prepared and used water bath (200 ml) of 20 and 40°C in post-coating treatments of the coating formed for 300 s, under ICP-AES investigation.

| Concentration (mg/l) | Zr  | Cr  |
|---------------------|-----|-----|
| As-prepared water bath | 0   | 0   |
| User water bath of 20°C | 0.007 (±0.0004) | 0.004 (±0.0007) |
| User water bath of 40°C | 0.001 (±0.0004) | 0.002 (±0.0005) |
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