Formation of a Trivalent Chromium Conversion Coating on AA2024-T351 Alloy

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The formation of a trivalent chromium conversion coating on AA2024-T351 aluminum alloy has been studied using electron microscopy, scanning Kelvin probe force microscopy, ion beam analysis and X-ray photoelectron spectroscopy (XPS). The coating contained oxide, hydroxide, fluoride and sulfate species, and consisted of two main layers: a zirconium- and chromium-rich outer layer and a thinner, aluminum-rich, inner layer. XPS indicated that zirconium and chromium are mainly present as ZrO2, Cr(OH)3, Cr2(SO4)3 and CrF3. In addition, a thin aluminum-rich layer, probably composed of hydrated alumina, occurred transiently at the coating surface. The coating above cathodic second phase particles was usually thicker than that above the matrix due to the locally increased alkalinity. In the early stages of treatment, the thickest coating formed above the S-phase particles. Localized corrosion and copper enrichment at the coating base. The localized corrosion is possibly related to the observed accumulation of fluoride ions at the inner layer and the enrichment of copper in the alloy. The thickness of the coating above the alloy matrix was significantly less than that of a coating formed on high purity aluminum.

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AA2024-T3 aluminum alloy is widely used in the aerospace industry due to its high strength to weight ratio and damage tolerance.1 However, the presence of copper as a primary alloying element leads to an increased susceptibility to localized corrosion, especially pitting corrosion.2,3 Hence, the alloy requires protective treatments to provide the required corrosion resistance for many applications. Such treatments often involve the use of chromate conversion coatings. However, the toxicity and high disposal costs of Cr(VI) wastes necessitate the development of eco-friendly alternatives.4,5

One promising candidate treatment uses a trivalent chromium bath, generally consisting of zirconium hexafluoride and trivalent chromium salts.6,7 The coating formation involves the dissolution of the native oxide on the aluminum surface due to the acidic, fluoride-containing solution,8 and the subsequent pH-driven deposition of zirconium and chromium species. The increase in interfacial pH is promoted by the cathodic reactions, i.e. hydrogen evolution and/or oxygen reduction.9 Previous work has indicated that the resultant coating consists of two layers.10,11 In one study, it was proposed that a first, dense layer is formed by hydrolysis of Cr(OH)x(3-x) and Zr(OH)y ions that retard oxidation of the alloy and reduce formation of Cr(III) in the coatings to form Cr(III) species.12 A second layer then forms by preferential deposition of zirconium hydroxide at transient cathodic sites.8 Other studies revealed a coating composed of an outer, hydrated zirconium-rich layer that also contains chromium species and an inner, aluminum-rich layer.7,9,10

Several investigations have been carried out to determine whether Cr(VI) species are formed in trivalent chromium conversion coatings. No Cr(VI) was detected by UV-visible spectroscopy in as-deposited trivalent coatings on AA2024 alloy, corroded panels, or in the coating solution.11 A similar result was obtained using Raman spectroscopic analysis of a freshly formed coating on the alloy.12 However, either an accelerated post-treatment or immersion in sodium chloride solution led to their presence.12 It was proposed that hydrogen peroxide, which is formed by reduction of oxygen at sites of copper-rich particles in the alloy, oxidizes the Cr(III) in the coatings to form Cr(VI) species.13 In contrast to the previous findings for as-formed coatings on AA2024 alloy, a recent investigation that employed Raman spectroscopy suggested the presence of Cr(VI) species in a coating formed on high purity aluminum.14

In the present study, scanning electron microscopy (SEM), transmission electron microscopy (TEM), ion beam analysis, scanning Kelvin probe force microscopy (SKPFM) and X-ray photoelectron spectroscopy (XPS) have been employed to investigate the kinetics of coating growth on second phase particles and the matrix of an AA 2024-T351 aluminum alloy and to determine the coating composition and the chemical states of coating species. The work reveals the preferential formation of the coating on second phase particles, with the initial coating growth being favored at S-phase particles. Further, the enrichment of fluoride ions and localized corrosion of the matrix at the base of the coating is disclosed, which has not been reported previously. The presence of fluoride ions in the coating prevents a firm conclusion to be reached on the presence of Cr(VI) species using XPS analysis due to the similarity of the Cr 2p binding energies of Cr(VI) and CrF3 species. The thickness of the resultant coating is shown to be significantly less than that of coatings formed on high purity aluminum.

Experimental

Specimen preparation.— AA2024-T351 alloy, with a composition of 4.65 wt% Cu, 1.54 wt% Mg, 0.52 wt% Mn, 0.21% Fe, 0.088 wt% Si, <0.5 wt% other elements, and bal. Al, was received as panels of 1.5 mm thickness. Specimens, with dimensions of either 30 × 24 mm or 30 × 12 mm, were cut from the panels, and cleaned with acetone, ethanol, and deionized water. Some specimens were then mechanically-polished to a 0.25 μm colloidal silica finish. Other specimens were ground to a 4000 SiC grit finish, followed by etching in 5 wt% NaOH for 60 s at 60 °C and desmutting in 50 v/v% HNO3 for 30 s at ambient temperature. All treatments were followed by rinsing in deionized water and drying in a cool air stream.

For the formation of the trivalent conversion coating, commercial SurTec 650 solution (SurTec Corp.) was diluted with deionized water to generate a 20 vol.% solution and the pH was adjusted to 3.9 by addition of 1 wt% NaOH. The etched and desmutted specimens were immersed in the SurTec 650 bath at 40 °C for 15, 30, 60, 120, 300 and 600 s; for the mechanically-polished alloys, immersion times of 15, 45, 60, 120 and 750 s were employed. All specimens were post-treated by immersion in deionized water at 20°C for 120 s, rinsing in deionized water, drying in a cool-air stream, and ageing for 24 h in laboratory air.

Specimen characterization.— The open circuit potential (OCP) of the mechanically-polished and the etched and desmutted AA2024-T351 alloy during 1200 s of coating formation was measured against a saturated calomel reference electrode (SCE) using a Solartec electrochemical workstation with a Modulab software controller. The exposed area of the coated surface was ~2.25 cm2. 
The compositions of the coatings were examined by energy-dispersive X-ray spectroscopy (EDS) in a Zeiss Ultra 55 scanning electron microscope at an accelerating voltage of 15 kV. In order to assess the coating formation on second phase particles, the intensity of the zirconium peak in EDS spectra at 2.1 keV was used as an indicator of the coating thickness, since zirconium is a main constituent of the coatings. All EDS data were processed using INCA software (version 4.09). A LEICA EM UC6 ultramicrotome was used to prepare electron transparent cross-sections of the specimens, with a nominal thickness of 30 nm, using a diamond knife. The cross-sections were observed by TEM in either a JEOL 2000 FX II instrument, operated at 120 kV in the bright field mode, or a FEI Titan G2 80-200 ChemiSTEM instrument, equipped with four EDS detectors, operated at 200 kV.

SKPFM, employing a Dimension 3100 microscope with a Nanoscope 3a controller (Bruker, Santa Barbara, USA), was used to record the variations of height and Volta potential on the alloy surface before and after the coating treatment. TESP2 tapping mode probes and OSCM-PT conductive probes for surface potential examination were used. A scanning rate was selected in the range from 0.5 to 1 Hz according to the area and roughness of the examined surface. Image data were processed using NanoScope off-line analysis software (Version 1.5).

RBS and NRA were employed to quantify the compositions of the coatings formed for 60, 120 and 300 s on the etched and desmutted alloy, using ion beams provided by the Van de Graaff generator at the University of Namur, Belgium. RBS employed 2 MeV \(^{4}\)He\(^{+}\) ions, incident normal to the specimen surface, with scattered ions detected at 165° to the direction of the incident beam. The data were interpreted using RUMP software. The carbon and oxygen contents of the specimens were assessed by NRA using the \(^{12}\)C(d,p)\(^{13}\)C and \(^{16}\)O(d,p)\(^{17}\)O reactions, employing 0.87 MeV \(^{4}\)He\(^{+}\) ions, with detection of the emitted protons at 150° to the direction of the incident beam. The oxygen contents were quantified to an accuracy of \(\pm 3\%\) using a reference specimen of anodized tantalum. Details of the analysis of \(^{16}\)O by NRA can be found elsewhere.\(^{14,15}\) The carbon content was estimated from the ratio of the yields of the \(^{12}\)C(d,p)\(^{13}\)C and \(^{16}\)O(d,p)\(^{17}\)O using literature values of the cross-sections for the respective reactions.\(^{16}\) The accuracy of the carbon analysis was \(\pm 20\%\). The region of analysis by RBS and NRA was of \(\sim 1\) nm diameter.

The composition of a coating formed for 300 s on the etched and desmutted alloy and the chemical states of coating species were investigated by XPS using a Kratos Axis Ultra DLD spectrometer (Kratos Analytical, U.K.), with monochromatic Al K\(_{\alpha}\) radiation (hv = 1486.6 eV), operated at 150 W and 1.0 \(\times\) 10\(^{-6}\) mbar. Data processing was carried out using CasaXPS version 2.3.17 (Casa Software, UK). Since the coatings are poor electron conductors, charging effects lead to an energy shift in the spectrum; thus, the binding energies were normalized to the carbon 1s peak of adventitious carbon at 284.6 eV. The area of the XPS analysis was \(\sim 700 \times 300\) \(\mu\)m.

**Results and Discussion**

**Coating morphology and growth kinetics.**—Figure 1 reveals the OCP during the treatments of both the etched and desmutted and the mechanically-polished specimens for 1200 s. The measurements of the potential-time curves were repeated three times with similar results. The potentials initially decrease relatively quickly to minimum values of \(\sim -0.99\) and \(-1.17\) V (SCE) for the respective pre-treatments after immersion times in the range 40 to 50 s. The rapid potential drop is probably associated with an initial thinning of the treatment solution. A second minimum occurs at times in the range 100 to 110 s, with potentials of \(-0.97\) and \(-1.29\) V (SCE) for the etched and desmutted alloy and the mechanically-polished alloy, respectively. It is later shown that at the time of the second minimum, the conversion coating has already been established on the matrix and second phase particles. The second minimum did not coincide with any significant changes in the coatings noticeable from the present compositional and morphological examinations. Hence, the reasons for its occurrence and for the difference in the minimum potentials for the two pre-treatments remain uncertain. After the second minimum, the potentials increased to \(\sim -0.82\) and \(-0.95\) V (SCE) after \(\sim 600\) s, with relatively little change thereafter. The latter potentials are \(\sim 400\) mV greater than that of relatively pure aluminum treated under similar conditions.\(^{13}\) The increased potential of the alloy is possibly related to the enrichment of copper in a thin alloy layer immediately beneath the coating, which is revealed by the TEM/EDS analysis that is presented later.

![Figure 1](https://example.com/image1.png)  
*Figure 1. The open circuit potential of the AA 2024-T351 alloy in the mechanically-polished, and etched and desmutted conditions during immersion in a dilute SurTec 650 bath at 40°C.*
The coating growth occurs at an average rate of ∼0.23 and 0.27 nm s⁻¹ up to 120 s, and then slows to ∼0.04 and 0.05 nm s⁻¹ from 120 s until the end of the treatments for the etched and desmutted alloy and the mechanically-polished alloy, respectively. In previous work, the decrease of the rate of coating growth has been attributed to reductions in both the mass transport through the coating and the alkalization associated with the cathodic reaction. Notably, the coating final thickness on the alloy is ∼50% of that achieved on high purity aluminum. The difference indicates a significant influence of the alloying additions on the coating formation. In the work of other investigators on coating formation on aluminum in a SurTec 650 bath, a coating thickness similar to that for in Fig. 3 for aluminum was obtained. They also reported a lengthy induction time of ∼100 s before growth of the coating commenced, which was not observed with the current treatment. However, the temperature of the coating bath, which was not specified in Ref. 8, may have differed between the studies.

The coating thicknesses above the S (Al₂MgCu), θ (CuAl₂) and α (Al-Cu-Mn) phases in the mechanically-polished alloy were assessed from SEM/EDS using the zirconium signal as a thickness indicator. Figures 4a and 4b show the zirconium peaks measured by point EDS analyses at the matrix and at S, θ and α second phase particles for coatings formed for 15 and 120 s, respectively. Zirconium was only detected in significant amounts above the S-phase particles after a treatment for 15 s. The greater thickness of the coating on the S-phase particles suggests an increased pH of the coating solution at these sites. However, after a treatment for 120 s, zirconium was detected at the matrix and all second phase particles. The highest zirconium content was recorded at the S-phase particle, as also found at 15 s, while the amounts of zirconium at the matrix and at the θ and α particles were similar. The zirconium peak recorded above the S phase increased progressively with treatment times of 15, 60, 120 and 750 s, as shown in Fig. 4c, which is consistent with the increasing coating thickness observed in the kinetics of Fig. 3. In contrast, the zirconium peak above the S phase showed no consistent trend with time, as shown in Fig. 4d, possibly due to either differing growth rates between different S-phase particles or detachment of the coating from some of the particles followed by re-growth of the coating.

Figures 5a and 5b display the scanning electron micrographs and EDS point analyses of the coating formed for 15 s above the θ- and S-phase particles (labelled I and II, respectively), revealing a relatively rough coating surface, which contains cracks, above the S phase. Whether the cracks were formed during coating growth of due to dehydration and shrinkage of the coating following subsequent ageing.

Figure 3. Dependence of the coating thickness above the matrix on time of coating formation for the etched and desmutted and the mechanically-polished AA 2024-T351 alloy treated in the dilute SurTec 650 bath at 40 °C. A comparison is made with the results of a previous study of coating formation on electropolished, high purity aluminum under the same conditions.13

| Time / s | Thickness / nm |
|---------|---------------|
| 0       | 0             |
| 100     | 20            |
| 200     | 40            |
| 300     | 60            |
| 400     | 80            |
| 500     | 100           |
| 600     | 120           |
| 700     | 140           |
| 800     | 160           |

Figure 2. Transmission electron micrographs of ultramicrotomed cross-sections of the etched and desmutted AA2024-T351 alloy following treatment in a dilute SurTec 650 bath at 40 °C for different times: (a) 15 s; (b) 60 s; (c) and (d) 120 s; and (e) 300 s. (f) A coating formed for 120 s on the mechanically-polished AA 2024-T351 alloy treated in the dilute SurTec 650 bath, which was not specified in Ref. 8, may have differed between the studies.

The coating thicknesses above the S (Al₂MgCu), θ (CuAl₂) and α (Al-Cu-Mn) phases in the mechanically-polished alloy were assessed from SEM/EDS using the zirconium signal as a thickness indicator. Figures 4a and 4b show the zirconium peaks measured by point EDS analyses at the matrix and at S, θ and α second phase particles for coatings formed for 15 and 120 s, respectively. Zirconium was only detected in significant amounts above the S-phase particles after a treatment for 15 s. The greater thickness of the coating on the S-phase particles suggests an increased pH of the coating solution at these sites. However, after a treatment for 120 s, zirconium was detected at the matrix and all second phase particles. The highest zirconium content was recorded at the S-phase particle, as also found at 15 s, while the amounts of zirconium at the matrix and at the θ and α particles were similar. The zirconium peak recorded above the S phase increased progressively with treatment times of 15, 60, 120 and 750 s, as shown in Fig. 4c, which is consistent with the increasing coating thickness observed in the kinetics of Fig. 3. In contrast, the zirconium peak above the S phase showed no consistent trend with time, as shown in Fig. 4d, possibly due to either differing growth rates between different S-phase particles or detachment of the coating from some of the particles followed by re-growth of the coating.

Figures 5a and 5b display the scanning electron micrographs and EDS point analyses of the coating formed for 15 s above the θ- and S-phase particles (labelled I and II, respectively), revealing a relatively rough coating surface, which contains cracks, above the S phase. Whether the cracks were formed during coating growth of due to dehydration and shrinkage of the coating following subsequent ageing.
in air and exposure to vacuum in the scanning electron microscope is uncertain. The preferential formation of the coating on the S phase is possibly owing to the presence of a copper-rich layer at the particle surface due to de-alloying of the particle that occurs rapidly upon immersion of the alloy in the coating bath. The copper-rich surface provides a preferential cathodic site, with the rise in pH favoring the deposition of coating material at this location. Coating material is also evident on the θ phase, although this appears to be thinner and finer textured compared with that on the S phase. Small zirconium-rich deposits, indicated by an arrow in Fig. 5a, were also observed on the coating surface; these have also been reported in previous work and may result from an instability of the coating solution. An example of a coating formed for 60 s on the mechanically-polished alloys above an α particle is shown in Fig. 6a. The coating thickness was ~28 nm, compared with ~35 and 20 nm at adjacent and remote regions of the matrix (Figs. 6b and 6c). The coating is probably thicker above the matrix near the particle than at the remote regions due to the increased pH generated at the former regions. The relatively similar thicknesses of the coating at the matrix and above the α phase particle is consistent with the similar intensities of the zirconium peaks for the two regions in the EDS analyses of Fig. 4d.

Examination of the effects of second phase particles on coatings formed for 15 s on the etched and desmutted alloy showed behaviours similar to those observed for the mechanically-polished alloy. The EDS analyses of Fig. 7a reveal the greatest zirconium signal intensity above an S-phase particle and a comparatively negligible intensity above θ and α particles and the matrix. Figure 7b shows the EDS analyses of the alloy after a treatment for 300 s, revealing a greater zirconium signal above the second phases than above the matrix. However, unlike the analyses for the mechanically-polished alloy treated for 300 s, there were negligible differences between the zirconium signals at the S, θ and α phases. The similarity of the analyses for the different second phases is possibly due to the influence of the etching pre-treatment, which leads to an enrichment of copper in the various types of the particles. The results for the mechanically-polished and the etched and desmutted alloy both indicate that the coating forms preferentially on the S-phase particles at the start of coating formation, which is supported also by the evidence of the surface morphology observed by SEM (Fig. 6).

The coating growth on second phase particles in the mechanically-polished alloy surface was also investigated by SKPFM. Table I reveals Volta potentials of the α, S and θ particles in the mechanically-polished alloy of ~200, 325 and 305 mV. The potentials decreased by ~50, 55 and 75 mV, respectively, following coating formation for 5 s. The decreases are probably due to activation of the alloy surface owing to thinning of the air-formed film following chemical attack by fluoride ions and the preferential deposition of coating material on the second phase particles. A treatment in the trivalent chromium bath for 15 s led to larger decreases of the Volta potential, by 140, 290 and 135 mV respectively, owing to the coating forming preferentially on the second phase particles. The larger decrease observed for S-phase particles is consistent with the relatively thick coating observed by SEM/EDS compared with the thickness of the coating on θ and α particles. After a treatment for 60 s, height and Volta potential maps

Figure 4. Energy-dispersive X-ray spectra at the matrix and S, θ and α phases following treatment of the mechanically-polished AA 2024-T351 alloy in the dilute SurTec 650 bath at 40°C for (a) 15 s and (b) 120 s. (c and d) Analyses at the matrix and S phase for the coatings formed for times from 15 to 750 s respectively.
Figure 5. (a) Scanning electron micrographs of the coatings formed in the dilute SurTec 650 bath at 40°C for 15 s at θ (I) and S phase (II) particles of the mechanically-polished AA 2024-T351 alloy; the arrow indicates zirconium-rich deposits. (b) EDS point analyses at points 1, 2 and 3 in (a).

Composition of coatings from TEM/EDS. — Figure 9 shows a TEM micrograph of a cross-section of the etched and desmutted alloy following a coating treatment of 60 s and the corresponding EDS maps of aluminum, oxygen, zirconium, chromium, fluorine, carbon, sulfur and copper. The micrograph reveals a coating comprising three layers. The outermost and innermost layers are of similar contrast, with thicknesses of \( \sim 4 \pm 1 \) and \( 3 \pm 1 \) nm respectively. The lighter intermediate layer has a thickness of \( \sim 10 \pm 1 \) nm. The EDS maps show that the innermost and outermost layers are aluminum-rich layers. These layers are separated by a thicker zirconium- and chromium-rich layer. Oxygen and fluorine are present throughout the coating. Carbon and sulfur appear to be mainly present in the zirconium- and chromium-rich layer. Copper is enriched in a thin alloy layer beneath the coating. Low concentrations of copper also appear to be present in the coating, and also of aluminum in the zirconium- and chromium-rich layer. The copper-rich layer shown in the TEM micrograph appears to consist of multiple bands. However, this is an effect of the orientation of the section to the electron beam and the roughness of the alloy/coating interface through the thickness of the section. The actual thickness of the layer, which is indicated by the thickness of one band, is \( \sim 2 \) nm, consistent with previous work.\(^{19}\) EDS mapping of the elemental composition, as shown in Figure 9, reveals no significant variations with respect to the potential of the matrix, due to the formation of a significant coating thickness on both the particles and matrix. The small regions of light appearance in the potential maps are zirconium-rich deposits, which were shown previously in the scanning electron micrograph of Fig. 5.
However, no significant presence of potassium was detected and increased concentration of potassium in the inner regions of the layer. Earlier work, using a different trivalent chromium bath, reported an enhancement of sodium is also present in the alloy and fluorine enrichment in the aluminum-rich innermost coat-

10 for a specimen coated for 300 s reveal copper enrichment in the alloy and fluorine enrichment in the aluminum-rich innermost coating layer. An enhanced concentration of sodium is also present in the layer. Earlier work, using a different trivalent chromium bath, reported and increased concentration of potassium in the inner regions of the coating. However, no significant presence of potassium was detected by EDS mapping in the present coating. The presence of the fluorine and oxygen species in the inner layer suggests that it may consist of a mixture of oxide, fluoride, oxyfluoride and possibly hydroxide species. The concentration of fluorine appears to be enhanced at regions of local corrosion of the alloy (indicated by arrows). At such regions, the enrichment of copper appears to be reduced compared with elsewhere along the alloy/coating interface.

Composition of coatings from RBS and NRA.— Figure 11 compares the experimental and simulated RBS data for specimens in the etched and desmutted condition before and following coating for 300 s. The etched and desmutted specimen displays a peak due to the enrichment of copper in the alloy that is generated by the pre-treatment process. This peak is displaced to lower energy for the coated specimen, since the enrichment now lies in the alloy immediately beneath the coating. The presence of the coating is indicated by peaks from zirconium and chromium. The main aluminum edge is displaced to a lower energy due to the presence of the zirconium- and chromium-containing layer. Small yields are evident from oxygen and fluorine in the coating. Hafnium is also detected, which is an impurity associated with zirconium. A two-layer model for the coating was sufficient to fit the data, with a zirconium-and chromium-rich outer layer and an aluminum-rich inner layer, which contained neither zirconium nor chromium. Both layers were simulated with the presence of oxygen and fluorine. Due to the limitation on the depth resolution of the analysis, the possibility of a very thin layer of hydrated alumina at the coating surface, as indicated by the TEM/EDS result of Fig. 9 for the specimen treated for 60 s, cannot be excluded. The RBS data indicated an upper limit on the layer thickness of ~3 nm.

The results of RBS analysis of the coating are given in Table II. A signal from sulfur in the coating could not be clearly resolved; the upper limit on the amount of sulfur in the coating was 5 × 10¹⁵ sulfur atoms cm⁻². Furthermore, a measurement of the copper content of the coating was prevented due to the relatively low concentration of copper and the background signal from the tail on the trailing edge of the zirconium peak. The tail was possibly due to the zirconium-rich particles that were observed on the surface of the coating. The hydrogen content of the coating cannot be determined by RBS, owing to the low mass of the hydrogen nucleus. The amounts of carbon and oxygen in the coating were determined by NRA, which provides a more accurate analysis of light elements than the RBS measurement. The carbon includes any surface contaminant picked up during the post-treatment of the specimen, which involved immersion and rinsing of the specimen in de-ionized water, and the subsequent exposure of the specimen to ambient environments, as well as any carbon incorporated into the coating from carbon-containing species that may be present in the SurTec 650 formulation. The amount of oxygen determined by NRA is higher than that determined by RBS. The difference in the results may be due to the accuracy of the respective methods or to variations in the coating thickness between the different regions of the specimen surface that were analyzed by RBS and NRA.

The RBS analysis revealed that chromium and zirconium in the outer layer of the coating occur in an atomic ratio of 0.45 ± 0.03. The ratio is similar to that determined for treatment of relatively pure aluminum in the same coating bath.₁³ A similar ratio was also measured for coatings formed on the present alloy for 60 and 120 s. A two-layer coating structure resembling that of the present coatings was also determined in other work that employed scanning Auger electron spectroscopy.₁₀ An hydrated zirconium-rich outer layer was present above a fluoroaluminate inner layer. The latter layer also contained potassium. The atomic ratio of chromium to zirconium was ~0.2, which is significantly lower than that in the present coatings. The difference in the coating compositions is probably due to the use of different commercial baths in the two studies.

The enrichment of copper in the alloy following etching and desmutting of the alloy was ~7.3 × 10¹⁵ copper atoms cm⁻² and 5.5 × 10¹⁵ copper atoms cm⁻² following a treatment of 300 s. The difference in the copper enrichment is probably associated partly with distributions in the coating was also carried out for specimens treated for 30, 120 and 300 s. A specimen treated for 120 s revealed elemental maps that were similar to those presented in Fig. 9 for the specimen treated for 60 s. However, the aluminum-rich layer at the coating surface appeared to be less uniform in thickness. In contrast, no aluminum-rich surface layer was resolved for specimens treated for either 30 or 300 s. The EDS maps of copper and fluorine in Fig. 10 for a specimen coated for 300 s reveal copper enrichment in the alloy and fluorine enrichment in the aluminum-rich innermost coating layer. An enhanced concentration of sodium is also present in the layer. Earlier work, using a different trivalent chromium bath, reported and increased concentration of potassium in the inner regions of the coating. However, no significant presence of potassium was detected.

Table I. Volta potentials on the second-phase particles relative to the matrix, investigated by SKPFM in the air, for the mechanically-polished AA 2024-T351 alloy and following coating of the alloy in a SurTec 650 solution at 40°C for 5 and 15 s.

| Species        | Bare alloy 5 mV | 15 s mV |
|----------------|-----------------|---------|
| θ-phase particles | 200 ± 20        | 150 ± 20 | 60 ± 20 |
| S-phase particles | 325 ± 25        | 270 ± 30 | 35 ± 15 |
| α-phase particles | 305 ± 20        | 230 ± 30 | 170 ± 25 |

Figure 7. Energy-dispersive X-ray spectra at the matrix and S, θ and α phases following treatment of the etched and desmutted AA 2024-T351 alloy in the dilute SurTec 650 bath at 40°C for (a) 15 s and (b) 300 s. Scanning electron micrographs of the coatings formed for (c) 15 s on an S phase particle (II) and (d) for 300 s on an α phase particle (III).
the roughness of the alloy/coating interface, which can lead to an underestimate of the enrichment. It is also possible that the copper enrichment was reduced following incorporation of copper into the overlying coating material. The average density of the coating was calculated from the composition and thickness of the coating formed for 300 s using the results of ion beam analysis and TEM respectively. The resultant value of $2.8 \pm 0.4 \text{ g cm}^{-3}$ compares reasonably with a value of $\sim 2.5 \text{ g cm}^{-3}$ for a coating formed on high purity aluminum.\textsuperscript{13}

**Composition of coatings from XPS.**— The results of XPS, determined from a low resolution spectrum, for the etched and desmutted alloy treated for 300 s, before and after correction for the presence of

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Figure 8. Height (left) and Volta potential (right) maps following treatment of the etched and desmutted AA 2024-T351 alloy following treatment in the dilute SurTec 650 bath at 40°C for 60 s. (a) $\alpha$-phase particle and (b) S- and $\theta$-phase particle clusters. Labels I, II and III labels indicate S-, $\theta$- and $\alpha$-phase particles.

Figure 9. High angular annular dark field transmission electron micrograph and EDS elemental maps of a coating formed on the etched and desmutted AA 2024-T351 alloy for 60 s in a dilute SurTec 650 bath at 40°C.
carbonaceous contamination,\textsuperscript{20} are given in Table III, which reveals the presence of aluminum, chromium, zirconium, copper, oxygen, fluorine, carbon and sulfur. The depth of analysis by XPS is limited to the outer $\sim 5$ nm of the specimen. The atomic ratio of chromium to zirconium was lower than that indicated by RBS, with a value of $\sim 0.31$ compared with $\sim 0.45$, possibly due to a difference in the near-surface composition of the coating relative to the coating bulk. In agreement with RBS, the XPS results indicate a much greater concentration of oxygen species compared with fluorine species, and a low content of sulfur. The XPS analysis also revealed a significant quantity of aluminum species and a low amount of copper species, both of which could not be detected by RBS. The aluminum species may be present in a surface deposit of hydrated alumina, as well as in the outer zirconium- and chromium-rich layer. A low concentration of copper may be expected in the coating, since copper can be incorporated into the coating above the matrix from the commencement of coating formation, as discussed later, and also at the locations of copper-rich, second phase particles.

The examination of the chemical states of coating species was carried out using high-resolution spectra for the Zr 3d and Cr 2p regions. An accurate analysis of the chemical states was not possible for aluminum, since the Al 2p peak was overlapped by peaks from Cr 3s and Cu 3p. In the case of copper, the signal was too weak to resolve individual species. Figure 12 shows the high resolution spectra from the Zr 3d photoelectron regions. Two spin orbit split doublets were separated by 3.1 eV in the Zr 3d photoelectron region, where the intensity ratio of Zr 3d$^5$/Zr 3d$^3$ was fixed at 1.5:1. The fitting of data was achieved using ZrO$_2$ and ZrF$_4$ species, with $\sim 97\%$ of the zirconium being present as oxide.

The high resolution spectrum of the Cr 2p$^3$/2 region, shown in Fig. 13a, was fitted by Cr(OH)$_3$ (577.3 eV), Cr$_2$(SO$_4$)$_3$ (578.5 eV), CrF$_3$ (580.1 eV) and Cr(VI) oxides (579.6 eV),$^{21,22}$ with 58, 32, 8 and 2\% of the chromium being the associated respective species. The sulfate probably originates from Cr$_2$(SO$_4$)$_3$ in the SurTec 650 formulation. The fitting does not provide conclusive evidence of Cr(VI) species, since the Cr(VI) peak used in the data fitting is not clearly

![Figure 10](image_url)

*Figure 10.* High angular annular dark field transmission electron micrograph and EDS elemental maps of a coating formed on the etched and desmutted AA 2024-T351 alloy for 300 s in a dilute SurTec 650 bath at 40°C.

![Figure 11](image_url)

*Figure 11.* Experimental and simulated (solid line) RBS spectra for the AA2024-T351 alloy in the etched and desmutted condition and following coating for 300 s in a dilute SurTec 650 bath at 40°C.

### Table II. Results of RBS and NRA analyses of a coating formed for 300 s on the etched and desmutted AA 2024-T351 alloy in a SurTec 650 solution at 40°C.

|        | Zr (x10$^{15}$ atoms cm$^{-2}$) | Cr | Hf | F | Al | O | O$_{\text{NRA}}$ | C$_{\text{NRA}}$ |
|--------|---------------------------------|----|----|---|----|---|-----------------|-----------------|
| 300 s  | 28.8                            | 13.1 | 0.2 | 61.0 | 13.7 | 124.7 | 141.8 | 30.8 |

### Table III. Results of XPS analyses of coatings formed on etched and desmutted AA 2024-T351 alloy in a SurTec 650 solution at 40°C for 300 s; (a) before and (b) after correction for a carbonaceous overlayer.

| Element | Zr (at.%) | Cr (at.%) | O (at.%) | Al (at.%) | S (at.%) | F (at.%) | Cu (at.%) | C (at.%) |
|---------|-----------|-----------|-----------|-----------|---------|---------|-----------|---------|
| Before  | 8.5       | 2.3       | 31.6      | 5.9       | 0.6     | 5.1     | 0.5       | 45.6    |
| After   | 19.7      | 6.2       | 51.8      | 8.7       | 0.9     | 9.9     | 0.9       | -       |

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resolved. If CrF₃ was not considered (Fig. 13b), fitting was achieved with ~7% of the chromium as Cr(VI), indicating that omission of CrF₃ form the data fitting leads to an overestimate of the possible Cr(VI) content of the coating. However, RBS showed that significant amounts of fluorine species were present in the coating, which suggests that the presence of CrF₃ must be considered. The formation of Cr(VI) in a coating after air ageing for at least 1 h has previously been shown to arise from oxidation of Cr(III) by H₂O₂ formed during oxygen reduction at copper-rich particles.⁶ Cr(VI) subsequently released from the coating to an aqueous environment can diffuse to provide corrosion inhibition at regions of bare alloy.²³

Formation mechanism of the coatings.— The formation of the zirconium- and chromium-rich coating layer occurs in response to an increase in pH due to the reduction of oxygen and hydrogen evolution. The pH change is enhanced at the second phase particles, which provide preferred reaction sites, resulting in an increased rate of coating formation at these locations. At the matrix, thinning of the air-formed oxide on the macroscopic alloy surface occurs initially, due to the presence of fluoride ions and the low pH of the trivalent chromium bath; the consequent electron tunnelling across the film enables the oxidation and reduction reactions to take place. The main oxidation process at the matrix region of the alloy, excluding hydration effects, is the oxidation of aluminum leading to the formation of amorphous alumina film according to the reactions:

$$2\text{Al} \rightarrow 2\text{Al}^{3+} + 6e$$

$$2\text{Al}^{3+} + 3\text{O}^{2-} \rightarrow \text{Al₂O₃}$$

The alumina may be hydrated in the outer regions. The continuation of the process requires the migration of Al³⁺ and/or O²⁻ ions across the alumina layer,³⁴ with Al³⁺ ions being ejected to the solution under low pH conditions. The alumina in the aluminum-rich inner layer of the coating is dissolved according to the reaction:

$$\text{Al₂O₃} + 6\text{HF} \rightarrow 2\text{AlF₃} + 3\text{H₂O}$$

The Al³⁺ ions released by dissolution of the alumina can diffuse through the coating to the solution, where they may precipitate as hydrated alumina, forming the aluminum-rich surface layer that was detected by EDS mapping. However, a significant thickness of hydrated alumina was only observed following treatments of 60 and 120 s. Furthermore, in a previous study, which also used TEM/EDS elemental mapping of coatings formed on high purity aluminum under conditions similar to those of the present work,¹³ no hydrated alumina layer was detected at the coating surface. Thus, it appears that the presence of the layer is a transient occurrence, which is possibly related to the local pH and concentration of Al³⁺ ions in the solution adjacent to the coating surface that control the deposition of the alumina and its subsequent dissolution. The solubility of alumina decreases significantly when the pH rises above about 4.²⁵ Li et al., using a microelectrode, observed that the pH at the coating surface

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Figure 12. High resolution XPS spectra for the Zr 3d photoelectron region and curve fitting for the etched and desmutted AA 2024-T351 alloy following immersion for 300 s in a dilute SurTec 650 bath at 40°C.

Figure 13. High resolution XPS spectrum for the Cr 2p photoelectron regions and curve fitting for the etched and desmutted AA 2024-T351 alloy following immersion for 300 s in a dilute SurTec 650 bath at 40°C.
increased from an initial value of 3.9 to 7.0 following a treatment of 120 s.18 The pH then reduced to 4 after a treatment of 600 s. In the case of the present coatings, it is suggested that the initial rise in pH and rate of generation of Al\(^{3+}\) ions resulted in a maximum thickness of hydrated alumina following a treatment of ∼60 s. Subsequently, the layer underwent a net thinning as the rate of formation reduced, since the coating growth limited the rate of diffusion of Al\(^{3+}\) to the coating surface, and the rate of dissolution increased, due to decreases in the pH and possibly also the fluoride concentration at the coating surface. Since the process is sensitive to the surface pH, variations in thickness of the hydrated alumina layer across the surface of a specimen may be anticipated, owing to the difference in local cathodic activity.

The growth of amorphous alumina films on Al-Cu alloys results in an enrichment of copper in the alloy immediately beneath the oxide film.6–8 In the case of the etched and desmutted alloy, enrichment is initially generated as a result of etching and maintained during desmutting. The level of copper enrichment depends upon the amount of copper in solid-solution in the alloy. Once the enriched layer is established, the aluminum and copper are incorporated into the alumina in proportion to their concentrations in the matrix. The enrichments of copper measured by RBS are equivalent to an average concentration of ∼30 to 40 at.% Cu in an enriched alloy layer of ∼2 nm thickness. During the formation of the alumina layer at the base of the present coating, the enrichment created during etching is expected to be sustained by the continuing formation of the alumina layer at the base of the coating. In the case of the mechanically-polished alloy, the enrichment of copper is initially negligible and the enrichment builds as the conversion coating is formed. Incorporation of copper into the coating is not expected to occur at the matrix regions during the enrichment process. Once sufficient enrichment of the alloy has been achieved, the copper is possibly incorporated into the coating on the alloy as nanoparticles of copper metal at the relatively low potential of the alloy in the SurTec 650 solution. In the case of the etched and desmutted alloy, nanoparticles may be generated from the start of the coating process. Once isolated from the substrate, the nanoparticles can be oxidized. The initial generation of the particles at the matrix regions may locally enhance the cathodic activity and have a role in the localized corrosion of the alloy. The delayed generation of nanoparticles for the mechanically-polished alloy possibly explains the reduced amount of localized corrosion compared with the etched and desmutted alloy. However, further work is required on the effects of the surface treatment on the coating growth to identify precisely the cause of the localized corrosion.

A comparison of the present results with earlier work of the authors shows that the atomic ratios of chromium to zirconium in the main layer of the coatings formed on the alloy and on high purity aluminum are very similar. Further, XPS analyses revealed similar chemical states of coating species on the two substrates, apart from the presence of copper species in the coating on the alloy. However, the rate of coating growth above the alloy matrix is slower than on the aluminum and the open-circuit potential of the alloy was ∼−400 mV higher than that during coating formation on the high purity aluminum. The increase in the potential for the alloy can increase the thickness of the alumina film at the base of the coating above the matrix by ∼0.4 nm, assuming that the alumina layer increases in thickness at ∼1 nm V\(^{-1}\), which is typical for amorphous alumina. The consequent reduction in the electron tunnelling through the alumina layer that sustains the cathodic reaction at the matrix regions during formation of the coating may explain the reduced rate of coating formation on the alloy in comparison with aluminum.

Conclusions

1. The coating formed on AA2024-T351 alloy in a SurTec 650 bath usually consists of two layers, comprising a main layer containing chromium and zirconium species, with an atomic ratio of chromium to zirconium of ∼0.45 ± 0.03, and a thinner, underlying aluminum-rich layer. A thin layer of hydrated alumina may also form at the coating surface. This layer reaches a maximum thickness in the early period of treatment and is thinned at later times in response to changes in the pH and Al\(^{3+}\) content of the solution adjacent to the coating surface.

2. The trivalent chromium conversion coating formation process on the alloy consists of the initial surface activation and preferential coating initiation on cathodic second phase particles. The thickest coating in the early stages of the coating process is formed on the S-phase particles that became cathodic through rapid de-alloying following immersion of the alloy in the low pH coating bath.

3. The coating growth on the alloy occurs at an average rate of ∼0.23–0.27 nm s\(^{-1}\) during the first 120 s of treatment, and then decreases to ∼0.04 – 0.05 nm/s. The coating thickness reaches ∼30 nm following a treatment of 600 s, which is approximately 50% of that achieved on high purity aluminum for the same treatment time.

4. Hydroxide, oxide, fluoride and sulfate species are present in the coating. Zirconium is mainly present as oxide, while chromium occurs mainly as hydroxide, sulfate and fluoride.

5. A copper-enriched layer is present in the alloy immediately beneath the coating and local regions of corrosion of the alloy occur at the base of the coating. The corrosion is associated with fluorine enrichment in the aluminum-rich layer at the coating base. The cause of the localized corrosion requires further investigation, but may be related to either the generation of copper nanoparticles from the copper-enriched layer or from influences of the alloy pre-treatment.

6. XPS data suggested the possible presence of a small amount of Cr(VI) species in the coating. However, the detection of small amounts of Cr(VI) by XPS is hampered by overlap with the yield from CrF\(_3\).

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