Role of Post-Treatment in Improved Corrosion Behavior of Trivalent Chromium Protection (TCP) Coating Deposited on Aluminum Alloy 2024-T3

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The effects of post-treatment applied on Trivalent Chromium Protection (TCP) coatings deposited on aluminum alloy 2024-T3 was studied by electrochemical and surface analytical techniques: X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The aim of the post-treatment was to improve the corrosion resistance of the TCP coating. To understand the influence of the post-treatment, using a bath containing H₂O₂ and a lanthanum salt as an inhibitor, our approach was to study the effect of these two components separately. It was found that the improved corrosion protection provided by the post-treated TCP was related to a synergistic effect of the two components. XPS and ToF-SIMS analyses showed that (i) the thickness of the TCP coating is not modified by the post-treatment, (ii) lanthanum is present on the surface and in the bulk of the TCP and (iii) is found in very small amount only on the external surface. The total concentration of Cr(VI) (oxide/hydroxide) was estimated to be below 0.1 wt% in the post-treated TCP layer. It was concluded that lanthanum plays a significant role in improving the coating density and homogeneity and has a beneficial effect on the TCP coating cracking as observed by Scanning Electron Microscopy.

Aluminum alloys are used for aerospace applications for their low weight and good mechanical properties. To improve the corrosion properties of aluminum alloys and to provide good paint adhesion, the first layer of coating applied on the aluminum alloy surface used to be a chromate conversion coating (CCC). However, hexavalent chromium used in the CCC coatings is highly toxic, and its use is very much restricted in Europe and the United States and will be forbidden by 2024 by the European Community with respect to the Registration, Evaluation, Authorization and Restriction of Chemicals (REACh). Therefore, new conversion coatings have been developed, and one of the most promising solutions is the Trivalent Chromium Protection coating called also as the Trivalent Chrome Process (TCP). TCP conversion coatings are formed by immersion in a solution containing Zr⁴⁺, Cr⁴⁺ and F⁻ ions, at a pH between 3.8 and 4.0. As it has already been widely discussed, the coating formation mechanism occurs by multiple chemical steps. The initial step involves dissolution of the aluminum oxide layer by fluorides. The removal of the oxide layer exposes the metal surface where cathodic reactions take place. Oxygen reduction reaction, and possibly hydrogen discharge, which counterbalance aluminum oxidation, consume protons and causes a pH increase at the interface between the metallic substrate and the solution, as measured by Li et al. The high pH favors the precipitation of ions present in the solution, forming a hydrated layer of zirconium and chromium oxide. The thickness of the TCP layer is usually of the order of 100 nm, depending on the nature of the aluminum alloy, the concentration of the solution and the immersion time.

TCP conversion coatings are amorphous, and have a two-layer structure as described by a majority of authors, with an outer part containing zirconium, chromium, oxygen and fluorine and an inner layer composed of aluminum, fluoride and oxygen. Although TCP has been designed to contain chromium only at a +3 oxidation state, some authors pointed out the presence of hexavalent chromium, while others indicate that only trivalent chromium was found. Hexavalent chromium has been detected on TCP after exposure to NaCl solution. Corrosion resistance provided by TCP conversion layers is widely discussed in the literature. TCP can potentially replace existing chromate conversion coatings, even if their corrosion resistance is inferior. Li et al. have shown that TCP coatings provide both anodic and cathodic protection by blocking physically Al-rich sites and copper-containing intermetallic particles. They also concluded that TCP offers a better corrosion protection to AA6061 and AA7075 than to the AA2024 aluminum alloys. Qi et al. pointed out, using Electrochemical Impedance Spectroscopy, that the corrosion protection of TCP is mainly ensured by the inner part of the layer and that the poor corrosion resistance of TCP coatings is related to their permeability, which allows for access of electrolyte to the substrate through the pores and cracks. The high polarization resistance (Rp value of 10⁷–10⁸ ohm-cm²) measured on the TCP coating by slow potentiodynamic polarization scans in 0.5 M Na₂SO₄ indicated some corrosion protection to AA2024 substrate but, according to Frankel et al., this is not enough to form an impermeable barrier. It was concluded that the TCP layer contains channels and pathways, through which dissolved oxygen can diffuse and reach the aluminum substrate.

There is a limited number of papers on post-treatments of TCP conversion coatings. Qi et al. studied a water immersion post-treatment on TCP formed on AA2024-T3. They found that the corrosion resistance of the coatings was the highest after post-treatment in the aqueous bath of pH 5 and the lowest for pH 9. The effect of phosphate post-treatment was studied on cerium conversion coating, and it was shown that the post-treatment can increase the corrosion resistance of the conversion layers.

The Socosurf PACS post-treatment (containing lanthanum nitrate salt and hydrogen peroxide with pH adjusted to a value between 4.2 and 5.3) was studied in this work. It was shown that the mean salt spray resistance (according to ASTM B117 standard) for a TCP without post-treatment is around 96 hours while it reaches 360 hours for a TCP after PACS post-treatment. The objective of this work was to understand how the PACS post-treatment modifies the conversion layer and improves its corrosion resistance. Our approach was to study the effect of two constituents of post-treatment bath separately:

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Experimental

Sample preparation.—A standard AA2024-T3 Aluminum Alloy was used in this research (provided by Rocholl GmbH). The 1.5 mm thick aluminum alloy sheet was cut into 1 cm² samples, ground and polished with alumina suspensions down to 0.3 μm. The polished samples were then cleaned ultrasonically in ultrapure water, isopropanol and ethanol for two minutes in each solution. After cleaning, the samples were degreased at 55°C for 20 minutes in a bath of diluted 10% (v/v) Sococlean A3432 solution (an alkaline silicate-free degreaser with pH close to 9). The degreased samples were immersed in ultrapure water for 1 minute and rinsed and then immersed in the Socosurf A1858/A1806 deoxidising solution (containing HNO₃, H₂SO₄ and Fe(III)) at 50°C for 5 minutes, with a pH < 1. The samples were then rinsed in ultrapure water for 1 minute and immersed for 5 minutes in the Socosurf TCS (Trivalent Conversion and Sealing) bath (containing a hexafluorozirconate and a salt of chromium(III) with an adjusted pH between 3.8 and 4.0) at 40°C to form the conversion coating (named here TCP layer). The coated samples were then rinsed in ultrapure water for 1 minute and immersed in the post-treatment solution Socosurf PACS (Passivation After Conversion and Sealing) containing lanthanum nitrate salt and hydrogen peroxide (adjusted pH to a value between 4.2 and 5.3) for 5 minutes at 25°C. The Socosurf TCS and Socosurf PACS solutions are commercialized by Socomore (France) under a licence of Mecaprotec (France).

In order to understand the effect of the Socosurf PACS post-treatment of the TCP layer on the corrosion properties of this system, two post-treatments baths were prepared: the first one denoted “lanthanum post-treatment” containing only a lanthanum nitrate salt and the second one, “hydrogen peroxide post-treatment”, containing only hydrogen peroxide. These solutions were used in the same conditions and compared with the Socosurf PACS: 5 minutes’ immersion time at 25°C, with pH adjusted between 4.2 and 5.3. These conditions have been chosen as optimal for the TCP post-treatment by industry. The samples were aged overnight in a desiccator prior to any surface or electrochemical characterization.

Electrochemical measurements.—Electrochemical measurements were performed at room temperature in a conventional three-electrode electrochemical cell with a saturated calomel reference electrode (SCE) and a platinum wire as the counter electrode. The potentiostat was an Autolab PGSTAT30. The working electrode area was delimited to 0.29 cm² by a Viton O-ring. The electrochemical measurements were carried out at room temperature in a 0.1 M NaCl aqueous solution, prepared with ultra-pure Millipore water and reagent grade chemicals (NaCl Analyar Normapur analytical reagent, VWR BDH Protabo). Linear Sweep Voltammetry (LSV) was performed from −1.1 V to −0.1 V vs SCE with a scan rate of 1 mV/s after 30 minutes of immersion at the open circuit potential (OCP). To ensure a good reproducibility, each electrochemical measurement was repeated three times under the same conditions.

Chemical and morphological characterization.—The surface chemical characterization was performed by means of XPS and ToF-SIMS using a VG ESCALAB 250 spectrometer and a ToF-SIMS V spectrometer (ION TOF GmbH – Munster, Germany), respectively.

For the XPS analysis, the base pressure in the analysis chamber was ∼10⁻¹³ mbar. Al Kα monochromatized radiation (hv = 1486.6 eV) was employed as the X-ray source. The spectrometer was calibrated against the reference binding energies (BE) of clean Cu (932.6 eV), Ag (368.2 eV) and Au (84 eV) samples. For all analyses, the take-off angle was 90°. High resolution spectra were collected with a pass energy of 20 eV. Data processing (peak fitting and deconvolution) was performed with the Advantage software version 5.966 provided by Thermo Electron, using a Shirley-type background and Gaussian/Lorentzian peak shapes at a fixed ratio of 70/30. Binding energies of the component peaks were corrected with reference to the CH₃CH₂ bonds set at 285.0 eV.

ToF-SIMS ion depth profiles have been used for chemical characterization for all samples. The ToF-SIMS analysis chamber was operated at pressure below ∼10⁻³ mbar. Ion depth profiles were recorded by interlacing a pulsed 25 keV Bi⁺ primary ion source delivering 1.2 pA of target current over a 100 × 100 μm² area with sputtering using a 2 keV Cs⁺ source beam delivering 100 nA of target current over a 400 × 400 μm² area. The same conditions were used for positive and negative ion profiles. For post-treated samples a cesium ion beam as a sputtering beam was used for formation of craters with well-controlled depths in order to perform the precise chemical characterization by XPS in the middle of each crater. In this case the Cs⁺ ion beam was used for sputtering (135 nA, 2 keV, 1000 × 100 μm²) and the analysis gun was Bi⁺ (1.2 pA, 25 keV, 100 × 100 μm²). The Bi⁺ primary ion flux below 10¹² ions/cm² was used to ensure static analysis conditions. Data acquisition and post-processing data analysis were performed using the Ion-Spec commercial software version 4.1. A Veeco Dektak 150 contact profilometer was used to measure the depth of each crater and to estimate the TCP layer thickness. The data were analyzed with the Dektak software.

Electrochemical measurements.—Figure 1 compares the OCPs and LSV polarization curves obtained in air-saturated 0.1 M NaCl electrolyte for aluminum alloy samples with TCP coatings without or with different post-treatments. As indicated in the experimental part, in order to understand the influence of different components of the industrial PACS post-treatment bath on the TCP coating, each component was studied separately: the hydrogen peroxide and the lanthanum salt.

For all samples (Figure 1a), regardless of applied post-treatment the OCP starts at a value between −0.52 and −0.55 V/SCE. The OCP remains relatively stable for the samples with the lanthanum post-treatment and the PACS post-treatment, with the final value of −0.55 V/SCE, after 1800 seconds of measurement. On the contrary, the OCP is decreasing for the two other samples. For the TCP without post-treatment, the OCP starts to decrease gradually from around 800 seconds, and reaches −0.72 V/SCE. A similar behavior (related to the OCP decrease after long immersion time in NaCl solution) was observed by Andreatta et al.,27 who reported that a Zr/Ti conversion coating (deposited on a AA6016 alloy) can retard the activation of the surface and the localized attack.

The lowest cathodic current can be detected for the sample with TCP coating with the hydrogen peroxide post-treatment as shown in Figure 1b. However, even this low cathodic current is observed, the overall corrosion behavior of H₂O₂-treated TCP layer is not enhanced with reference to the non-treated TCP layer, due to not improved anodic current and pitting potential. For the other samples (without post-treatment, with lanthanum and with PACS post-treatments), no significant decrease of the cathodic current is observed. The lowest value of the cathodic current can be observed for the TCP coating with the PACS post-treatment confirming the effect of small cathodic inhibition. Anodic plateaus are observed for all samples. The curve recorded after lanthanum post-treatment shows the shortest anodic
Figure 1. (a) OCP versus time and (b) LSV polarization curves (scan rate = 1 mV/s) performed in 0.1 M NaCl (pH = 6) on the AA2024 covered by TCP conversion layers without post-treatment and after PACS, lanthanum or hydrogen peroxide post-treatments.

Plateau. Higher anodic currents in the plateau region \((\approx 3 \times 10^{-6} \text{ A/cm}^2)\) can be observed for the samples without post-treatment and with the hydrogen peroxide post-treatment, while for the sample with the lanthanum \((\approx 7 \times 10^{-7} \text{ A/cm}^2)\) and PACS \((\approx 5 \times 10^{-7} \text{ A/cm}^2)\) post-treatments, the anodic currents are between 4 and 6 times lower, respectively. The lowest anodic current is observed for the sample with the PACS post-treatment.

\(E_{\text{corr}}\), measured from the LSV polarization curves, shows the lowest value \(E_{\text{corr}} = -0.79 \text{ V/SCE}\) for the TCP submitted to \(\text{H}_2\text{O}_2\) post-treatment. However, the low corrosion potential can be attributed to low cathodic current and does not always indicate the high corrosion susceptibility. Slightly higher \(E_{\text{corr}} \approx -0.70 \text{ V/SCE}\) for the sample without post-treatment can be related to its higher cathodic current, with reference to the sample with \(\text{H}_2\text{O}_2\) post-treatment. The samples with lanthanum and PACS post-treatments show the highest \(E_{\text{corr}}\) values of \(-0.58 \text{ V/SCE}\) and \(-0.55 \text{ V/SCE}\), respectively, which may indicate the best corrosion resistance.

Another parameter used for evaluation of the corrosion resistance is the pitting potential, \(E_{\text{pit}}\). \(E_{\text{pit}}\) is around \(-0.51 \text{ V/SCE}\) for the samples without post-treatment and with the hydrogen peroxide and lanthanum post-treatment, while the highest \(E_{\text{pit}}\) of \(-0.45 \text{ V/SCE}\) is observed for the PACS post-treatment. It can be then suggested, that the displacement of the \(E_{\text{pit}}\) to higher potentials indicates better pitting corrosion resistance. Thus, in the case of PACS post-treatment, the best corrosion resistance can be evidenced by higher \(E_{\text{pit}}\), with reference to other samples and the decrease of both cathodic and anodic currents. The best pitting corrosion resistance for the PACS post-treated sample was also confirmed by the accelerated corrosion tests (according to ASTM B117 standard) as indicated in the introduction part.

**Surface and in-depth chemical characterization of TCP coatings without and with post-treatment.**—Figure 2 shows the ToF-SIMS depth profiles obtained on aluminum alloys coated with a TCP without post-treatment (a and c) and after PACS post-treatment (b and d). Both the negative ion depth profiles (a and b) and after PACS post-treatment (b and d). Both the negative ion depth profiles (a and b), which are commonly used to study oxide species,\(^{28-31}\) and the positive ion depth profiles (c and d) to study the metallic (lanthanum, zirconium and chromium) species were measured. The same sputtering conditions have been used for all the samples in the negative and positive mode, allowing for a direct comparison. ToF-SIMS ion-depth concentration profiles are presented here as a function of etching time. However, the sputtering time was also recalculated vs the sputtering depth using a profilometer measurements as indicated in the experimental part. The ion intensity is reported using a logarithmic scale in order to magnify the low intensity signals.

In the negative ion depth profiles (Figures 2a and 2b), the represented profiles are for the following ions: \(\text{ZrO}_2^-, \text{CrO}_2^-\), \(\text{AlO}_2^-\), \(\text{AlO}_2^+\) and \(\text{Al}_2^+\). For oxygen analysis, the \(\text{O}_2^-\) isotope signal was used instead of \(\text{O}_2\), which saturates the detector. The intensities of each ion are plotted as a function of the sputtering time. The changes in ion intensities with the sputter time reflect in-depth variations in concentration, but are strongly dependent on the matrix from which the ions are emitted.\(^{32}\) Due to different sputtering yields of different secondary ions, no quantitative analysis related to the coating composition can be obtained by ToF-SIMS as it is possible with XPS.

Three main regions can be identified in the negative ion depth profiles presented in Figures 2a and 2b. In the first region, the plateaus of \(\text{ZrO}_2^-, \text{CrO}_2^-\), \(\text{AlO}_2^-\), \(\text{AlO}_2^+\) and \(\text{Al}_2^+\) ions are attributed to the TCP conversion layer. As the conversion layer is mainly composed of zirconium and chromium oxides, the \(\text{ZrO}_2^-\) and \(\text{CrO}_2^-\) ions signals are used to define the boundaries of the TCP conversion layer. The end of the TCP conversion layer is marked by the end of the plateaus and the decrease of \(\text{ZrO}_2^-\) and \(\text{CrO}_2^-\) signals, measured at around 620 ± 20 seconds and 630 ± 20 seconds for the TCP without post-treatment (Figure 2a) and the TCP after PACS post-treatment (Figure 2b), respectively. The second region characterized by an increase of \(\text{AlO}_2^-\) and \(\text{AlO}_2^+\) signals is an interfacial region corresponding to the inner part of the TCP conversion layer. The third region corresponds to the metallic substrate where \(\text{Al}_2^+\) (characteristic of the presence of metallic aluminum) signal reaches a plateau. The width of this region is 920 ± 20 seconds and 955 ± 20 seconds for the TCP without post-treatment (Figure 2a) and the TCP after PACS post-treatment (Figure 2b), respectively.

ToF-SIMS positive ion profiles, recorded on the same samples, have been mainly used to determine the distribution of lanthanum in the conversion layer after PACS post-treatment. In the positive ion depth profiles (Figures 2c and 2d), the plotted ions are \(\text{Cr}^+, \text{Zr}^+\) and \(\text{La}^+\). Since the same sputtering conditions have been used for negative and positive profiles, the sputtering time corresponding to the thickness of the conversion layer defined in negative mode is the same in positive mode: 620 ± 20 s and 630 ± 20 s for the TCP without post-treatment (Figure 2c) and with PACS post-treatment (Figure 2d). Slightly longer sputtering time of around 40 s observed for the plateau of \(\text{Zr}^+\) in the case of the positive profile on TCP (Figure 2c) than in the case of the negative profile can be related to the local differences of thickness and/or roughness of the conversion layer.

As expected, no significant amount of lanthanum was detected in the TCP sample without the post-treatment (Figure 2c), since lanthanum is a constituent of the post-treatment solution, and not the TCP solution. This very low signal intensity (around 10 counts) was
registered due to very low detection limit of the ToF-SIMS technique in the ppb range. In Figure 2d, a strong La$^+$ ion intensity signal is measured over 200 seconds of sputtering, then it decreases steadily until around 450 seconds, and then a sharper decline can be observed after 450 s until reaching a minimum at about 870 seconds of sputtering. These results indicate that lanthanum is present in the whole TCP layer, with, however, a lower amount in the inner part of the TCP layer.

The conversion layer thicknesses were determined by coupling the ToF-SIMS negative ion depth profiles with the profilometry measurements of the crater depth. The mean value of the sputtering rate on TCP conversion layers (repeated on ten samples) is 0.28 nm/second ($\pm$ 0.02 nm/second) calculated with parameters specified in the experimental part. The thicknesses for both samples (presented in Figures 2a and 2b) are almost identical, being 173 $\pm$ 6 nm (620 $\pm$ 20 s of sputtering) and 176 $\pm$ 6 nm (630 $\pm$ 20 s of sputtering) for the TCP without and with post-treatment, respectively.

The chemical composition of TCP conversion layers with different post-treatments has been measured by XPS. The results are presented in Table I. The TCP conversion layers are mainly composed of zirconium oxides, hydroxides and fluorides; chromium oxides and hydroxides and possibly fluorides and fluoroaluminates. A low intensity of aluminum signal corresponding to metal and oxide was detected on all samples but the quantification was not attempted because of the difficulty to distinguish the aluminum oxide present in the conversion layer and the aluminum oxide present on the coated alloy substrate (in the coating cracks). The formation and presence of cracks will be discussed in the following part. The metallic aluminum and a part of the aluminum oxide detected by XPS originate from the aluminum alloy substrate not covered by the TCP layer. The presence of cracks can be explained by sample exposure to high vacuum conditions in the XPS analysis chamber and the coating dehydration, which leads to the coating cracking$^{11,33}$.

The oxygen/fluorine ratio ranges from 4.7 to 9.1 (Table I). The post-treated TCP samples exhibit a higher oxygen/fluorine ratio

| Composition (% at.) | TCP | TCP + La | TCP + H$_2$O$_2$ | TCP + PACS |
|---------------------|-----|----------|------------------|------------|
| O                   | 66  | 68       | 73               | 66         |
| F                   | 14  | 12       | 8                | 11         |
| Zr                  | 15  | 15       | 14               | 12         |
| Cr                  | 5   | 3        | 5                | 4          |
| La                  | 0   | 2        | 0                | 7          |
| O/F                 | 4.7 | 5.7      | 9.1              | 6.0        |
can be concluded that the principal component is La2O3 or La(OH)3 and is rapidly turned into hydroxide La(OH)3 when exposed to air.38,39

The binding energies of these components are in good agreement with values reported in the literature for chromium oxide34,42,48 and chromium hydroxide.5,34,43,49

As discussed before, the binding energy of 577.1 eV can be attributed to CrO3, and a symmetric peak at 577.3 eV (FWHM = 2.8 eV) attributed to Cr(OH)3. The binding energies of these components are in good agreement with values reported in the literature for chromium oxide and chromium hydroxide.5,12,34,43,47,48

Figure 3 presents the core level spectra of Cr2p with the spin orbit doublet: Cr2p3/2 and Cr2p1/2 for a TCP without post-treatment (a), and TCP with PACS post-treatment (b). For the sake of clarity, the results obtained for the samples with only La or only H2O2 post-treatment are not presented here. Interpretation of the chemical environment of chromium from the Cr2p spectra gave rise to numerous discussions proposing different ways of data interpretation.12,40–46 From these papers, different important points should be taken into account when interpreting the Cr2p peak. The choice of the background subtraction method can impact the qualitative and quantitative analyses.32,42 Therefore, Cr(III) oxide species should be represented by a multiplet splitting or an asymmetric broadening peak and not by a single, symmetrical peak.42 According to Biesinger et al.43 Cr(III) oxide shows discrete multiplet structure whereas the hydroxide shows only a broad peak shape, and a single peak is used for Cr(VI) compounds (no unpaired electrons). Another difficulty to interpret the chemical environment of chromium is a very close binding energy of Cr(VI) species (between 579.5 eV and 580.2 eV) and Cr(III) attributed to CrF3 (between 579.3 eV and 580.8 eV).34 Therefore, in fluoride containing materials, such as TCP conversion coatings, the distinction between Cr(VI) species and Cr(III) attributed to CrF3 is difficult. The peak attribution and discrimination between different chromium compounds was recently discussed by Qi et al.12

In the case of Cr2p spectrum obtained for the TCP coated sample without post-treatment (Figure 4a), a broad peak is observed in the area of Cr2p3/2, which can be fitted with two components: an asymmetric peak at 576.3 eV (with FWHM of 2.4 eV) attributed to Cr2O3, and a symmetric peak at 577.3 eV (FWHM = 2.8 eV) attributed to Cr(OH)3. The binding energies of these components are in good agreement with values reported in the literature for chromium oxide and chromium hydroxide.5,12,34,43,47,48

Figure 4b presents the Cr2p spectra obtained for the TCP coated sample with PACS post-treatment, where two peaks are clearly distinguished at binding energies of 577.1 eV (FWHM = 2.7 eV) and 579.8 eV (FWHM = 1.9 eV). The lower binding energy peak at 577.1 eV can be decomposed into two peaks at 576.3 eV and 577.3 eV corresponding to chromium oxide and hydroxide, respectively. The higher binding energy peak, observed at 579.8 eV is attributed to Cr(VI).5,34,43,49

As discussed before, the binding energy of 577.8 eV could correspond to both Cr(VI) and CrF3. However, as no peak was observed at this binding energy on a TCP sample without post-treatment (Table I), a high quantity of CrF3 after post-treatment seems unlikely. Therefore, it is concluded that the peak observed at
579.8 eV is due to the presence of hexavalent chromium (Cr(VI)) in a form of chromium oxide or hydroxide. As aforementioned, the results obtained for the samples with only La or only H$_2$O$_2$ post-treatment are not presented here, but as expected, the La post-treatment has no influence on the shape of the Cr2p core level spectra, whereas the H$_2$O$_2$ leads to Cr2p peak enlargement and appearance of new component at higher binding energy attributed to Cr(VI).

In depth composition of post-treated TCP conversion coating.— As reported above, the XPS analysis revealed the presence of Cr(VI) and lanthanum at the surface of TCP conversion layers with PACS post-treatments and which show the improved corrosion behavior. In order to have a better insight into the improved corrosion performance of the coating with the PACS post-treatment, a more detailed study, combining ToF-SIMS sputtering and depth profiling with XPS surface characterization, was undertaken. The aim was to evaluate the surface and in-depth chemical composition of the coatings, including the in-depth distribution of Cr(VI) species. Figure 5a presents a schematic cross section of the AA 2024-T3 sample coated with the TCP conversion layer with PACS post-treatment, where three locations for XPS analysis were prepared by ToF-SIMS depth sputtering using a Cs$^+$ ion beam (135 nA, 2 keV, 1000 $\times$ 1000 $\mu$m$^2$): (i) non-sputtered extreme surface, (ii) craters at a depth of 10 nm, (iii) another crater at a depth of 40 nm. The samples prepared in the ToF-SIMS chamber were then transferred from the ToF-SIMS to the XPS analysis chamber in a sealed container under argon atmosphere, using the glove-boxes connected directly to the ToF-SIMS and the XPS spectrometers, in order to avoid sample contamination or oxidation. Argon ion beam sputtering is known to lead to reduction of different compounds i.e. Cr(VI) to Cr(III). A similar phenomena of reduction can be induced by the Cs$^+$ ion sputtering, however the sputtering by cesium ions is less energetic than by argon ions. Therefore, if a reduction occurs with the Cs$^+$ beam, it would affect only the extreme surface of the sample (less than 2 nm in depth). Thus, even with a possible reduction process occurring at the extreme surface (maximum 2 nm), it would be possible to measure by XPS the coating composition below this thickness (under the 2 nm of depth), not impacted by the Cs$^+$ ion beam sputtering. Another advantage of the Cs$^+$ ion beam sputtering performed in the ToF-SIMS is a very precise depth control of each crater. The XPS analysis area was 500 $\times$ 500 $\mu$m$^2$, centered in each spot of 1000 $\times$ 1000 $\mu$m$^2$ prepared by Cs$^+$ ion sputtering in the ToF-SIMS analysis chamber.

Figures 5b and 5c present the Cr2p and La3d core level spectra obtained for the non-sputtered surface area and at depths of 10 and 40 nm. The XPS analysis performed on the extreme surface (non-sputtered surface) shows two distinct peaks in the Cr2p3/2 core level spectra indicating the presence of both Cr(III) and Cr(VI) (as shown above in Figure 4b, and discussed in details previously). The XPS analyses performed in the areas of both craters (10 and 40 nm) show only a broad Cr2p3/2 peak at binding energy of 576.4 $\pm$ 0.1 corresponding to Cr(III). The slightly lower binding energy of Cr(III) observed at the bottom of the craters (inside the coating) than on the extreme surface of the TCP coating with PACS post-treatment (as discussed in previous part and shown in Figure 4) may originate from the presence of a higher Cr$^{3+}$ oxide/hydroxide ratio. There is no detectable signal at higher binding energy, indicating that no Cr(VI) is present (Figure 5b). The interpretation of the Cr2p spectrum is difficult because the binding energies of Cr(VI) and oxyfluoride of Cr(III) are very close. A low signal intensity at a binding energy of 579.8 eV can be observed so the presence of hexavalent chromium in the craters cannot be ruled out. It is possible to calculate the maximum quantity of Cr(VI) present at different depths of the layer (in each crater), and therefore calculate the maximum quantity of Cr(VI), which could be present in the TCP layer after PACS post-treatment. To do so, a peak at a binding energy of 579.8 eV with a FWHM of 2.0 eV is used to represent Cr(VI) (Figures 6a and 6b). These fitting parameters are the ones used for the Cr(VI) peak...
Figure 6. High resolution XPS core level spectra of Cr2p in the 10 nm crater (a) and the 40 nm crater (b). A peak at a binding energy of 579.8 eV with a FWHM of 2.0 eV is used to evaluate the maximum quantity of Cr(VI) that the sample could contain. A schematic cross section of the AA2024 aluminum alloy sample with TCP conversion layer with PACS post-treatment is presented (c) to calculate the maximum concentration of Cr(VI).

on the surface, where the presence of Cr(VI) is not questioned. In the 10 nm deep crater (Figure 6a), the peak attributed to Cr(VI) represents 3% at. of the total Cr peak. At this depth, the quantity of chromium is 5.5% of the TCP layer deep. So if Cr(VI) is present in this 10 nm deep crater, it represents less than \( \sim 0.2\% \) at. of the TCP layer. Using the same reasoning, we conclude that if Cr(VI) is present in the 40 nm deep crater it represents less than 0.1% at. of the TCP layer. On the outer surface (10 nm), the peak attributed to Cr(VI) was clearly identified (Figure 4b) and Cr(VI) represents 3% at. of the TCP layer. From all these data (summarized in Figure 6c) the maximum quantity of Cr(VI) has been calculated and represents 0.3% at. of the post-treated TCP layer. Considering a 1 mm thick aluminum alloy AA2024-T3 sheet covered by this layer, the maximum Cr(VI) quantity that could be found on this sample is \( \sim 4 \times 10^{-5} \) wt%, which is much below the 0.1 wt% concentration of Cr(VI) authorized by the REACh regulation.

Figure 5c reveals that lanthanum is present both at the surface and inside the coating. However, it can be noticed that its quantity decreases with depth. This result is in agreement with the ToF-SIMS data presented above (Figure 2d). La3d5/2 on the extreme surface is observed at a binding energy of 835.5 eV, and it shifts to lower binding energy of around 834.4 eV in the spectra recorded in the two craters (Figure 5c), which can be attributed to the difference of hydroxylation between the extreme surface and the bulk conversion layer as observed and discussed previously for the chromium compounds.

As lanthanum and hydrogen peroxide are the two components of the PACS post-treatment solution, it was expected to find lanthanum and hexavalent chromium in the coating (as a result of oxidation of Cr(III)). However, the results (Figures 5b and 5c) demonstrate the presence of Cr(VI) only at the extreme surface of the conversion layer while lanthanum is found both at the surface and inside the coating.

Figure 7. SEM images obtained on AA2024-T3 with TCP (a) without post-treatment, (b) after PACS post-treatment, (c) after lanthanum post-treatment, and (d) after hydrogen peroxide post-treatment. The samples were aged overnight in a desiccator prior to SEM analysis.
The rapid decrease of the OCPs observed for the samples without any post-treatment and with H₂O₂ post-treatment (Figure 1a) suggests a higher electrochemical activity of the aluminum alloy substrate, which can be exposed through the coating defects and pores to the aggressive chloride ions present in the electrolyte. In contrast, the stable OCP observed for the PACS and the lanthanum post-treatments applied on the TCP coatings indicates that these post-treatments are beneficial for the corrosion behavior. These two post-treatments seem to stabilize the TCP layer and to block the access of aggressive chloride ions to the aluminum surface. This can indicate an improvement of the barrier properties of the TCP layer after lanthanum containing post-treatments. The highest Eₘ₉₀ and the lowest anodic currents (Figure 1b) observed for the samples with TCP with lanthanum and PACS post-treatments indicate also the improved corrosion performances. The improved corrosion protection provide by the PACS post-treatment is confirmed by the highest Eₘ₉₀ (Figure 1b). The improved properties can be assigned to the synergistic effects of both components present in the post-treatment solution: hydrogen peroxide and lanthanum.

The ToF-SIMS results (Figures 2a and 2b) indicate that the PACS post-treatment does not modify the thickness of the TCP conversion layer (173 ± 6 nm and 176 ± 6 nm for the sample without and with PACS post-treatment, respectively). Therefore, the improved corrosion properties of the post-treated samples, as evidenced by electrochemical results, are not related to the layer thickness. The ToF-SIMS results show the presence of the lanthanum in the bulk of the post-treated TCP layer and the decrease of the oxygen/fluorine ratio, which can lead to a better corrosion resistance as is usually expected from an oxide than from a fluoride. The XPS characterization indicates that on the surface of the PACS post-treated sample, the lanthanum is in the form of La(OH)₃, however the presence of a small content of La₂O₃ or LaF₃ cannot be ruled out. After PACS post-treatment, the XPS analysis evidences the presence of Cr(VI) principally at the extreme surface of the TCP conversion layer, which can be explained by an oxidation of the Cr(III) oxide by the hydrogen peroxide present in the post-treatment bath. As discussed in the bibliographic part, the oxidation of Cr(III) and formation of Cr(VI) was already evidenced on the TCP coating after exposure to NaCl electrolyte or even after exposure to air. The self-healing effect of hexavalent chromium has been discussed in numerous papers, and is thought to be one of the main reasons for the good corrosion behavior of chrome conversion coatings. The hexavalent chromium present in the chrome conversion coating would be able to migrate to the defects in the conversion layer where it would be reduced to Cr(III), forming a protective layer on the defect. However, here, the post-treatment brings also lanthanum as a corrosion inhibitor to the TCP layer, which is present on the surface and in the coating bulk as evidenced by ToF-SIMS depth profiles (Figure 2d). Rare-earth inhibitors, particularly cerium and lanthanum, are among the most studied inhibitors for replacement of hexavalent chromium. Lanthanum acts as a cathodic inhibitor and forms a dense and protective layer of lanthanum hydroxide on intermetallic particles. Based on the information obtained from the combined ToF-SIMS in-depth profiling and XPS analysis, related to the presence of lanthanum and hexavalent chromium in the bulk and on the extreme surface of conversion layer, a mechanism for the PACS post-treatment can be proposed. The PACS solution penetrates inside the pores and defects of the TCP conversion coating. The obtained results show that lanthanum is retained inside the conversion layer, probably in the pores and defects. The formation of La-rich TCP layer filling the layer defects present in the entire conversion coating over the matrix and the IMPs can be assumed. Hydrogen peroxide would also penetrate in the defects and pores, but Cr(VI) can be formed only when hydrogen peroxide is in contact with Cr(III). As discussed above, the quantity of Cr(III) in the conversion coating is limited and represents only a 4% of TCP coatings (Table 1). Therefore, a major- ity of the Cr(III) present in the conversion layer is not exposed to the hydrogen peroxide, and only the Cr(III) present at the surface and in the coating pores can be oxidized. A very small amount of Cr(III) (present in the pores) is exposed to peroxide, which explains why hexavalent chromium is not detected inside the coating. However, inside the coating, the presence of a small quantity of Cr(VI), below the detection limit of the XPS, cannot be excluded. Decreasing the TCP coating porosity by application of post-treatment can have a strong (beneficial) influence on the corrosion resistance. It may hinder the penetration of chloride ions into the bulk of the coating, and prevent the initiation of localized corrosion. Thus, the combination of two factors: presence of Cr(VI) at the surface and lanthanum blocking the coating pores improves the corrosion resistance of the TCP coating.

As demonstrated by SEM (Figure 7) the PACS post-treatment significantly limits the cracking of the conversion layer. The high vacuum to which a sample is exposed during a SEM experiment can trigger an accelerated drying, which creates these mud-like cracks. The formation of these cracks under vacuum was followed in an environmental SEM by Laget et al. 13 on a chrome conversion coating and by Guo et al. 11 on a TCP. Both studies conclude that the conversion layer is free of cracks when freshly formed, and that cracks develop because of accelerated drying under vacuum. Our work does not demonstrate the link between the susceptibility to cracking of the conversion layer under vacuum and its corrosion resistance, as has been established by other researchers. Laget et al.3 studied chrome conversion coating, and concluded that the dehydration of the coatings explains the losses in corrosion resistance observed after aging. Heller et al.65 found that inhibiting cracking improves the corrosion resistance of cerium conversion coatings but that elimination of cracking alone does not guarantee a good corrosion protection. They conclude that the corrosion protection of cerium conversion coating depends on both the surface morphology and the chemical composition of the coating. Therefore, it is believed that the improvement of the corrosion resistance of the TCP after PACS post-treatment is partly due to the reduced cracking of the TCP conversion layer after post-treatment.

The most probable hypothesis to explain the action of the post-treatment is that it seals the TCP conversion layer and blocks its defects limiting the accelerated dehydration. The fact that the post-treatment containing only lanthanum is able to limit the cracking also strengthens this hypothesis. The stable OCP observed on TCP after lanthanum containing post-treatment is also consistent with a sealing effect of lanthanum.

### Conclusions

The objective of this work was to study the effect of a post-treatment on TCP conversion coatings, and to determine the role of each of its two components (lanthanum salt and hydrogen peroxide) in the improvement of the corrosion resistance of TCP layers. The main findings are:

1. A synergistic effect of the two components was observed, neither of the constituents separately is able to provide a corrosion protection equivalent to the post-treatment with both components.
The thickness of the TCP conversion coating was not modified by the PACS post-treatment.

After PACS post-treatment, Cr(VI) was detected on the surface, but not inside the conversion layer. The total concentration of Cr(VI) in the post-treated TCP layer was estimated to be below 0.1 wt%.

Coupling ToF-SIMS and XPS allowed for a chemical analysis of the bulk of the TCP layer and revealed only the presence lanthanum and quasi-absence of hexavalent chromium. Therefore, a mechanism for the PACS post-treatment was proposed: a penetration of post-treatment solution inside the pores and defects of the TCP layer, with a possible accumulation of lanthanum and limited formation of hexavalent chromium due to scarce resource of trivalent chromium reacting with H₂O₂. As a result, the amount of hexavalent chromium was below the detection limit XPS. The sealing effect of lanthanum was also suggested by the SEM results.

The three post-treatments studied (lanthanum or hydrogen peroxide alone and PACS) affected the oxygen/fluoride ratio of the TCP layer. More oxide and less fluoride detected after post-treatments could have a positive influence on the corrosion resistance of the TCP conversion layer.

The post-treatment diminished the susceptibility to cracking of the TCP conversion layer. This beneficial effect on cracking is attributed to lanthanum sealing of pores and defects.

The better corrosion resistance of a post-treated TCP compared to a TCP without post-treatment was attributed to a combination of sealing provided by lanthanum and the presence of two inhibitors (hexavalent chromium and lanthanum) on the post-treated coating surface.

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