Chromate Formed in a Trivalent Chromium Conversion Coating on Aluminum

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This present study employs aluminum substrates to investigate the formation of Cr(VI) species during a trivalent chromium conversion coating process. The study had a particular focus on understanding the influences of copper in the substrate and O2, ZrF62− and F− in the bath on the formation of Cr(VI) species, which were detected by Raman spectroscopy. Comparison of electropolished aluminum and sputtering-deposited aluminum substrates revealed greatly increased rates of coating growth associated with an enrichment of copper impurity in the electropolished substrate that was revealed by transmission electron microscopy. With respect to chromium chemistry in a developed coating, the presence of dissolved oxygen and long conversion treatment times promoted the formation of Cr(VI) species that are generated by oxidation of Cr(III) species. The Cr(III) species are oxidized by H2O2, which was produced by oxygen reduction reaction. The generation of H2O2 was demonstrated by analysis of the treatment bath using UV spectrophotometry.

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Conversion coating processes are employed as surface pre-treatments of aluminum and aluminum alloys to improve the adhesion with organic primers and increase corrosion protection. Chromate conversion coating (CCC) has been widely used as a conventional and effective process in the aerospace and automotive industries.1–3 However, the toxicity of chromates to human beings and the detrimental impact of their use.4,5 In contrast, trivalent chromium species are relatively eco-friendly and, hence, trivalent chromium conversion (TCC) coating processes are being investigated as promising alternatives to CCC processes.6

The TCC coating bath generally contains hexafluorozirconate, sodium fluoride and trivalent chromium sulfate, which results in coatings formed on aluminum that contain Zr-/Cr-rich oxides, hydroxides and fluorides.7–8 Interestingly, a freshly-formed TCC coating after a conversion treatment for 1200 s in a naturally-aerated bath displayed chromate presence by a Raman shift at 866 cm−1, but the peak intensity was negligible in a coating formed in a deoxygenated bath.7 Notably, the oxidation of Cr3+ to Cr6+ in the aqueous electrolyte is not due solely to the presence of dissolved oxygen. This conclusion is supported by experiments in which no significant chromate species were found in the solution bubbled with only air for more than 300 h.9 In contrast, the Cr3+/Cr6+ reaction has been reported to occur in atmospheric oxygen at high temperature during a bush fire10 and also with the presence of MnO2 oxidant in the natural sea water.11,12 In the case of TCC coatings, chromate formation has been attributed to the transient formation of hydrogen peroxide generated by oxygen reduction. The influence of H2O2 has been explored by Li et al.13 who immersed TCC coated AA2024 alloy in 0.5 M Na2SO4 solutions with addition of 0.01, 0.1 and 1 v/v % H2O2 for 1 h. A small level (0.01% v/v) of H2O2 can significantly promote the formation of chromate species and Raman intensities associated with chromate species increased in proportion to the concentration of H2O2. However, the investigation of the role of H2O2 in the absence of H2O2 additions is not an easy task.

In addition, the influence of the substrate composition on H2O2 formation and, hence, chromium chemistry, is also of relevance. Chromate species have been locally detected on the coated particle surface, but not above the coated matrix, in the situation of AA2024 (Al-Cu) alloy substrate.13 The chromate was associated with coating cracks around the protruding particles, which provide channels for oxygen diffusion and, hence, increase the cathodic reaction of oxygen reduction to form H2O2. For the reaction mechanism, it was still unknown and required the future research. In comparison with the localized chromate species in the coated AA2024 alloys, the high-purity aluminum (99.998% purity) after coating for 1200 s displayed a homogeneous existence of chromate species across the coating. This differing chromate population would correlate with high reactivity of aluminum, although a thin copper-enriched layer was observed on the base of coated aluminum.8 In order to validate this hypothesis, the present study prepared a sputtered Al layer on high-purity aluminum foil to develop the trivalent chromium conversion coatings on the surface. The associating chemical analyses were performed by Raman spectroscopy.

Based on the assumption that the generation of chromate species is directly related to the hydrogen peroxide formation, the influence of substrate composition (copper and aluminum), conversion treatment duration, and solution chemicals (F−, ZrF62−, Cr3+) on the formation of H2O2 in TCC coatings has been comparatively studied by analytical electron microscopy, Raman spectroscopy and UV spectrophotometry.

Experimental

Materials and reagents.—Specimens of dimensions of 30 × 12 mm were cut from aluminum sheet of 0.3 mm thickness, with a composition of 50 ppm Cu, 20 ppm Fe, 10 ppm Mg, 480 ppm Si and bal. Al. This measured composition was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), using a Pekin-Elmer Optima 5300 dual view instrument. They were then rinsed in acetone, ethanol and deionized (DI) water (pH 6.5, resistivity 18 MΩ cm) and electropolished in a mixture of 60 wt% perchloric acid and 80 v/v % ethanol (1:4 v/v, <10°C) at 20 V for 4 min. After this, electropolished aluminum was rinsed in ethanol and then DI water for 15 s respectively and dried in a stream of cool air. Aluminum layers of 400 nm thickness were then deposited on the electropolished aluminum in an Atom Tech Ltd. magnetron sputtering system, using an aluminum target (99.999% purity). The system was first evacuated to a pressure of 2 × 10−4 Pa. The sputtering process was then carried out in 99.999% argon at 0.5 Pa for 1 h. The specimens were stored in the drying cabinet filled with silica gel. The prior pre-treatment to TCC coatings includes DI water rinsing and drying in a stream of cool air.

SurTec 650 chromitAL (SurTec Corp.) is a commercial trivalent chromium solution, was diluted with DI water in 1:4 by volume. The solution was then adjusted to pH 3.9 by adding 5 wt% H2SO4 and 1 wt% NaOH droplets. TCC coatings were formed by immersing

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Table I. Codes used to designate solutions used for studying the effect of solution chemicals on generation of H$_2$O$_2$ during the TCC treatment of aluminum.

| Solution codes | Compositions |
|---------------|-------------|
| Acid (pH 3.9) | H$_2$SO$_4$, pH 3.9 |
| F- + Acid     | 0.01 M NaF, pH 3.9 |
| KZF + Acid    | 0.01 M K$_2$ZrF$_6$, pH 3.9 |
| Cr(III) + F + Acid | 0.01 M Cr(NO$_3$)$_3$, 0.01 M NaF, pH 3.9 |
| Cr(III) + KZF + F + Acid | 0.01 M Cr(NO$_3$)$_3$, 0.015 M K$_2$ZrF$_6$, and 0.01 M NaF, pH 3.9 |

The coating morphologies were investigated by scanning electron microscopy (SEM), using a Zeiss Ultra 55 instrument with an energy-dispersive X-ray spectroscopy (EDS) facility, operated only at an accelerating voltage of 15 kV. A JEOL 2000 FX II transmission electron microscope, with an accelerating voltage of 120 kV, was used to examine the electron transparent thin cross sections of specimens with a nominal thickness of 30 nm that were prepared by ultramicrotomy with a diamond knife. In order to examine the copper-rich layer at the coating/substrate interface, diffraction patterns were collected by an FEI Tecnai 300 transmission electron microscope. Diffraction data were processed by Digital Micrograph (TM) software (version 3.6.5).

In order to examine the coating chemistry across the TCC coatings, a Renishaw 2000 Raman instrument with a 514 nm argon laser excitation was used and controlled with GRAMS/32 programme and WIRE Video view software. The integration time was 30 s, with 10 times accumulation to avoid the effect of stray light noise. Prior to the specimen examination, the argon laser was calibrated using a standard silicon panel at 520 cm$^{-1}$. Raman spectra were collected over the frequency range of interest between 1200 and 200 cm$^{-1}$.

The surface topographies under ambient conditions were recorded by a multimode Nanoscope SPM in contact mode and a Dimension 3100 microscope was employed with Nanoscope 3a controller (Bruker, Santa Barbara, USA). The TESPA tapping mode probes used in the present study were with a force constant of ~42 N/m and a resonance frequency of ~320 kHz. The data were processed by Nanoscope Analysis software (version 1.5).

Results and Discussion

Coatings formed on electropolished aluminum.—A transmission electron micrograph of the electropolished aluminum after conversion treatment in SurTec 650 chromiAL solution for 60 s, followed by immersion in DI water at 40°C for 120 s and drying in a stream of cool air, is shown in Figure 1a. The micrograph reveals a conversion coating with a thickness of ~18 nm thick attached to the aluminum substrate. A dark band, with a thickness in the range 1 to 5 nm, at the coating base suggests the presence of an enrichment of copper that was contained in solid solution in the original aluminum sheet. The band is revealed by the mass/thickness contrast with the underlying aluminum and with the coating material. An electron diffraction pattern recorded in the area outlined by a red circle in Figure 1a, which is located at the dark band, is presented in Figure 1b. The diffraction pattern originated from (111) planes of the aluminum matrix (in red) and the (020) plane of the tetragonal θ phase (Al$_2$Cu; a = 0.404 nm and c = 0.58 nm); the latter plane confirms the presence of an enrichment of copper. The copper enrichment is formed by preferential oxidation of aluminum with copper accumulating beneath the oxide film that is present on aluminum during the electropolishing process; the enriched layer typically has a thickness about 2 nm, similar to that shown in the micrograph of Figure 1a.

Eventually, sufficient copper is accumulated for both aluminum and copper atoms to be oxidized and thereafter a relatively constant amount of copper (measured as the number of copper atoms per unit area) is maintained in the enriched layer. Since the solid solubility of copper in aluminum at room temperature is only 0.02 atom %, the Al$_2$Cu phase can be formed when the copper content is sufficient. The variable thickness of the dark band in Figure 1a is due to the large thickness of the ultramicrotomed section, which was nominally 30 nm, compared with the thickness of the copper-enriched layer, and to the fine scale roughness at aluminum/coating interface. Thus, the enriched copper is not contained in one plane through the section thickness. The reason for the copper enrichment requires the future research and one reason is due to the electropolishing treatment which removes a greater thickness of the copper-enriched layer and with the coating material. An electron diffraction pattern originated from (111) planes of the aluminum matrix (in red) and the (020) plane of the tetragonal θ phase (Al$_2$Cu; a = 0.404 nm and c = 0.58 nm); the latter plane confirms the presence of an enrichment of copper. The copper enrichment is formed by preferential oxidation of aluminum with copper accumulating beneath the oxide film that is present on aluminum during the electropolishing process; the enriched layer typically has a thickness about 2 nm, similar to that shown in the micrograph of Figure 1a.

Specimen characterizations.—The open circuit potential (OCP) of sputtered aluminum specimens was measured during coating formation for 1200 s in the naturally aerated SurTec 650 chromiAL solution, using a Solarton electrochemical workstation with a Module lab software controller. A conventional three-electrode cell was employed containing a saturated calomel reference electrode (SCE, 0.24 V vs. NHE), a platinum wire as a counter electrode and the working electrode with the exposed area of ~2 cm$^2$. The reproducibility of the data with errors of less than 3%. A cuvette was used to contain a standard silicon panel at 520 cm$^{-1}$. Raman spectra were collected over the frequency range of interest between 1200 and 200 cm$^{-1}$.

In order to determine the influence of various solution chemicals in the conversion coating bath on the generation of H$_2$O$_2$, aluminum specimens, of dimensions 30 × 20 × 0.3 mm, were immersed in each of the solutions listed in Table I. The pH value of each solution was adjusted to 3.9 by adding droplets of 5 wt% H$_2$O$_2$. The Cr(NO$_3$)$_3$, pH2O, NaF, K$_2$ZrF$_6$, H$_2$SO$_4$, NaOH, H$_2$O$_2$, and K$_2$O$_2$Ti$^2$H$_2$O (labelled as titanyl reagent) were purchased from Sinopharm Chemical Reagent Co. Ltd., China and were of analytical grade. The last solution in Table I (Zr/Cr atomic ratio = ~0.7) simulated the composition of the SurTec 650 chromiAL solution. Specimens were first ground to a 1200 SiC grit finish, followed by etching in 5 wt% HCl at room temperature for 5 s and rinsing in DI water for 15 min. Five specimens were immersed in 250 ml of each solution at 40°C; the solution was contained in a glass beaker and was magnetically stirred. The warm temperature at 40°C is the same with the condition of the previous TCC coating formation in SurTec solutions, and this is used to avoid the interference of solution temperature with the conclusions. The stirring treatment of all solutions is to enhance mass and electron transport for the reaction at the substrate/solutions interface to promote the formation kinetics of hydrogen peroxide.

For the colorimetric measurement of H$_2$O$_2$ by the titanyl method, a mixture solution of 3 M H$_2$SO$_4$, 0.05 M CaK$_2$O$_3$Ti and DI water of 1:1:4 by volume was used. All measurements were repeated the times under the same conditions (including the sample pre-treatment and tested solutions) in order to ensure good reproducibility of the data with errors of less than 3%. A cuvette was used to contain a mixture of 1 ml of the test solution (Table I) and 2 ml of titanyl reagent. The former was collected after reaction of the aluminum in the various solutions for 0, 300, 600, 1200, 1800, 3600 and 5400 s. A UV-vis spectrophotometer (UV-3000, MAPADA) was employed to investigate the absorbance at 400 nm within 20 min of collection in the cuvette. Notably, the special amounts of hydrogen peroxide at 0, 20, 50, 100, 200, 500 and 1000 μM were prepared to complete the spectrophotometric calibration measurement, using 1 ml H$_2$O$_2$ and 2 ml titanyl reagent. Results revealed a standard concentration curve as follows, H$_2$O$_2$ concentration (μM) = 2950 × A$_{400}$ (A$_{400}$-absorbance). Based on the standard formula, the H$_2$O$_2$ concentration in the reaction solutions can be calculated step by step. Prior to each measurement, the spectrophotometer was calibrated by using deionized water sample. The reproducible data were recorded by triplicated measurements under the same conditions and the relative error was less than 3%.

Specimen characterizations.—The open circuit potential (OCP) of sputtered aluminum specimens was measured during coating formation for 1200 s in the naturally aerated SurTec 650 chromiAL solution, using a Solarton electrochemical workstation with a Module lab software controller. A conventional three-electrode cell was employed containing a saturated calomel reference electrode (SCE, 0.24 V vs. NHE), a platinum wire as a counter electrode and the working electrode with the exposed area of ~2 cm$^2$. The reproducibility of the data with errors of less than 3%.
indicating aluminum oxides, and the spectrum for 1200 s was taken from our previous paper (Fig. 2e).\(^8\) Cr(III) species in the form of hydroxide, fluoride and oxide are represented by Raman shifts at 536–540 cm\(^{-1}\), while the fingerprint of Cr(VI) species is located at 845–866 cm\(^{-1}\).\(^{14}\) In addition, zirconium oxide, aluminum oxide and sulfate-containing compound (e.g. Cr\(_2\)(SO\(_4\))\(_3\)) yield Raman shifts at 470, 804 and 998 cm\(^{-1}\) respectively.\(^{14,20}\) Thus, the major components of the TCC coatings, which consist of oxides, hydroxides and fluorides of zirconium and chromium, are identified by Raman shifts in the range 400–600 cm\(^{-1}\).\(^8,14\) With respect to TCC coatings formed for 30 and 60 s (Figs. 2a and 2b respectively), Raman intensities at 400–600 cm\(^{-1}\), due to chromium and zirconium species, were negligible since the coatings were too thin (~18 nm after 60 s according to TEM). These coating components were of too low concentrations to be detected by Raman signals. This work first reveals a Raman limit for coating components in a thin film and Raman investigation is effective when the coatings are formed for more than 300 s. In addition, Raman characteristic of chromate species was detectable at 866 cm\(^{-1}\) in coatings after conversion treatments for 1200 and 1800 s. This revealed that a long conversion treatment time is an important factor influencing chromate formation.

**Coatings formed on sputtering-deposited aluminum.**—Figures 3a and 3b display transmission electron micrographs of the sputtering-deposited aluminum layer (a) in the as-deposited condition and (b) following conversion treatment in the SurTec 650 chromitAL solution for 1200 s followed by immersion in DI water at 40°C for 120 s and drying in a stream of cool air. The initial thickness of the aluminum layer was ~400 nm; the thickness of the subsequently-formed conversion coating was ~57 nm. In contrast, according to TEM measurements of a previous study, the thickness of a coating formed for 1200 s on electropolished aluminum under the present coating
conditions was $\sim 155$ nm. Thus, an increase in the coating thickness by a factor of about three was revealed in comparison with the coating formed on the sputtering-deposited aluminum. Low- and high-magnification scanning electron micrographs and associated EDS point analyses of coating surfaces on the sputtering-deposited aluminum are presented in Figures 4a, 4b and 4c respectively. Figure 4b corresponds to the area outlined by a red square in Figure 4a. Notably, the coated surface displayed the presence of round nodules of up to $\sim 400$ nm diameter; in some instances, these were associated with cracks in the adjacent coating. The presence of coating cracks is consistent with the observation made in a previous study of coatings formed on electropolished aluminum. 2 SEM/EDS spectra in Figure 4c revealed peaks due to zirconium, chromium, oxygen and fluoride components and a large peak due mainly to aluminum substrate beneath the thin coating. Notably, the spectra were similar at locations of particles and at the adjacent coating, since the interaction volume of the X-rays is significantly larger than the particle size. This is also supported by the strong peak intensities of aluminum in both spectra.

A transmission electron micrograph of the sputtering-deposited aluminum after a conversion treatment for 60 s is shown in Figure 5a; the film is only several nanometers thick. The associated electron diffraction pattern in Figure 5b, recorded at the circled area in Figure 5a, revealed (111) FCC aluminum. In comparison, the coating on electropolished Al after the same conversion treatment was 18 nm thick. Hence, a much thinner coating was generated on the sputtering-deposited aluminum. The absence of cathodic copper impurities on the surface of the sputtering-deposited aluminum is considered to be the main reason for the difference in the coating kinetics.

Figure 6 shows Raman spectra of the sputtering-deposited aluminum prior to conversion treatment (Figure 6a) and after conversion treatment for 1200 s in naturally-aerated and deoxygenated baths (Figures 6b and 6c respectively). For the bare substrate (Figure 6a), a primary Raman shift at 804 cm$^{-1}$ can be attributed to an aluminum oxide/hydroxide film on the aluminum surface. In Figures 6b and 6c, the major coating components, in the form of zirconium and chromium oxides, were detected in both coated specimens by Raman shifts at 470 and 536 cm$^{-1}$ respectively. In addition, Raman shifts at 998 cm$^{-1}$ are associated with sulfate components such as chromate sulfate. Notably, a distinct and characteristic Raman shift at 866 cm$^{-1}$ occurred in the coatings formed in a naturally-aerated bath (Figure 6b), indicative of the presence of Cr(VI) species. In contrast, for TCC coatings formed in a deoxygenated bath no shifts in the range 840–904 cm$^{-1}$, due to that Cr(VI) species were resolved (Figure 6c). Hence, the availability of dissolved oxygen appears to be necessary for oxidation of Cr(III) species, which is consistent with the findings of our previous work using electropolished aluminum.

Interestingly, Raman investigation effectiveness for the chemical components reveals a positive dependence on the coating thickness, which is determined by the conversion treatment duration and substrate. The coatings formed for 60 s on electropolished Al was $\sim 18$ nm, which, however, displayed the undetectable Raman peaks of Zr-/Cr-rich components. In contrast, the effective coating
thickness should be $\sim 80$ nm after conversion treatment for 300 s, which displayed the evident Raman peaks for such coating components as shown in Figure 2c. In terms of the coatings formed on the sputtering-deposited Al, Raman spectrum in Figure 6b clearly reveals the coating components. The coating thickness was $\sim 57$ nm and is the lowest required thickness for the Raman effectiveness in the present study. This relationship between substrate and coating thickness and/or Raman effectiveness needs the future discussion in depth.

The open-circuit potentials of the sputtering-deposited aluminum during conversion treatment for 1200 s in the naturally-aerated and deoxygenated baths are shown in Figure 7. In the naturally-aerated bath, the OCP initially fell and then gradually increased to a relatively steady level after immersion for about 400 s. The minimum potential, which was reached after about 200 s, and the final potential were $-1.48$ and $-1.45$ V$_{\text{SCE}}$ respectively. A previous study of the OCP during conversion treatment of electropolished aluminum in a naturally-aerated bath indicated that the time to reach the minimum potential was about half as long as that for the sputtering-deposited aluminum. This correlates with the faster kinetics of coating formation on the electropolished surface that were indicated by the earlier TEM results. For the de-oxygenated bath, the potential fell more rapidly and revealed two minima, with values of $-1.51$ and $-1.50$ V$_{\text{SCE}}$ at times of 15 and 75 s, before reaching a relatively steady potential of $-1.45$ V$_{\text{SCE}}$ after 122 s. The steady potentials of the sputtering-deposited aluminum in both aerated or deoxygenated baths were similar, and also similar to that found in a previous study for electropolished aluminum.

Notably, the earlier Raman results revealed that Cr(VI) species were present in the coatings formed on both substrates after conversion treatment for 1200 s in naturally-aerated solutions. Evidently, Cr(VI) formation is primarily dependent on the presence of dissolved oxygen in the conversion treatment bath. In contrast, it is not significantly affected by the presence of a copper-enriched layer in the substrate, which was only observed for the electropolished aluminum substrate. In addition, the copper-containing intermetallic particles surrounded by aluminum matrix revealed a significant difference in morphology, structure and copper content with the copper-enriched layer formed on electropolished aluminum.

Atomic force microscopy (AFM) was used to examine the topography of sputtering-deposited aluminum and the electropolished aluminum prior to TCC treatments as shown in Figures 8a and 8b respectively. The latter result was referred to our previous work as described in Ref. 8. The columnar nanocrystals of dimension of hundreds of nanometres and the voids of depth up to 30 micrometres (outlined by red arrows) were presented in Figure 8a. This incompact surface is due to a physical sputtering process and also determines a relatively fast kinetics of surface dissolution with more rapid fall of initial open-circuit potential as discussed above. In contrast, the highly-ordered furrows were investigated in the form of (110) Al in Figure 8b, and it was attributed to the preferential adsorption of alcohol molecules on surface ridges. Furthermore, the chemically pH-driven deposition of TCC coating formation has been reported in our previous study, where the coating initiation displayed the same process on the metal ridge and interval valleys. As a consequence, the furrowed surface morphology was still faintly visible in the coated surface after conversion treatment for 300 s. In this sense, the surface topography variance between two substrates might have an effect on the difference of the initial OCP values, and an incompact surface of sputtering-deposited samples with more rapid fall of initial open-circuit potential was revealed compared to the electropolished surface.

**H$_2$O$_2$ measurements.**—With respect to conversion reaction during coating formation, electrons are generated by aluminum oxidation, Al $\rightarrow$ Al$^{3+}$ + 3$e^-$. Interestingly, a constant rate of aluminum dissolution of $\sim 0.11 \pm 0.02$ nm/s along the surface subjected to conversion treatment was reported in our previous study using atomic probing microscopy. The continuous availability of free electrons at the solution/metal interface can promote the formation of highly reactive hydroxyl radicals (HO$_2$ ⋅), as described in Ref. 27. The formation of hydroxyl or hydroperoxy radicals and hydrogen peroxide is suggested to occur as follows, (O$_2$)$_{\text{ads}}$ + $e^- \rightarrow$ O$_2$ ⋅ or (O$_2$)$_{\text{ads}}$ + $e^- + H^+ \rightarrow$ HO$_2$ ⋅; HO$_2$ ⋅ + HO$_2$ ⋅ $\rightarrow$ H$_2$O$_2$ + O$_2$. Following the above reactions, H$_2$O$_2$ in the solution adjacent to the metal surface was produced. Furthermore, a previous hypothesis for the formation of Cr(VI) species in fresh TCC coatings was based on the formation of HO$_2$ during the conversion treatment. In order to support this hypothesis, Figure 9 displays the dependence of the H$_2$O$_2$ concentrations, determined by the colorimetric method, on the reaction time in the different naturally-aerated environments listed in Table 1.
and also in DI water, at a temperature of 40°C. Notably, the tested solutions were obtained from the reaction solutions in which the mechanically polished aluminum specimens were immersed. In addition, low concentrations associated with low absorbance through reaction solutions in the short reaction time may be associated with the matrix effect, which quantitative values were not involved in the present paper. The reproducibility of resultant data was achieved by triplicated measurements under the same conditions, which relative error was less than 3%.

For DI water (pH 6.5) and H_2SO_4 solution (pH 3.9), very low H_2O_2 concentrations were measured even after the prolonged immersion for up to 5400 s. However, an addition of 0.01 M NaF to the H_2SO_4 solution (pH 3.9) significantly increased the H_2O_2 concentration and then rose up to ~170 μM H_2O_2 at 5400 s. The fluoride ions present in the H_2SO_4 solution promoted the dissolution of the oxide film on the aluminum surface. As a consequence, the rate of aluminum oxidation was considerably enhanced by enabling increased electron tunnellings through the oxide to support the oxygen reduction.28,29 The acceleration of oxygen reduction resulted in a large increase in H_2O_2 generation relative to immersion in the DI water and the fluoride-free H_2SO_4 solution. In contrast, immersion in the H_2SO_4 solution containing fluoride added as 0.015 M K2ZrF6 resulted in a more moderate increase in the kinetics of H_2O_2 generation; after reaction times of 300 and 5400 s, the H_2O_2 concentrations were much lower compared with the addition of NaF. The decrease in H_2O_2 amounts that are generated in the K2ZrF6-containing solutions is associated with the complex fluoride chemistry. Chidambaram et al.30 revealed that the complex fluoride ions did not effectively attack the surface oxide, while the single fluoride ion was directly involved in thinning of the oxide. However, the hydroxide ions generated by the cathodic reaction can promote the hydrolysis of hexafluorozirconate ions, which results in release of F− ions and formation of zirconium hydroxide,31,32 according to the reaction:

\[
\text{ZrF}_6^{2−} + 4\text{OH}^- \rightarrow \text{ZrO}_2 \bullet 2\text{H}_2\text{O} + 6\text{F}^- \tag{1}
\]

The released F− ions were available to thin the alumina film and enhance the oxygen reduction reaction and zirconium hydroxide may deposit on the surface as reported by Chidambaram et al.30 Immersion in the H_2SO_4 solution that contains additions of 0.01 M Cr(NO3)3, and 0.01 M NaF, resulted in a final H_2O_2 concentration similar to that produced in the H_2SO4 solution containing only an addition of NaF. However, at early times of immersion, up to about 1000 s, the H_2O_2 concentration was lower in the solution containing 0.01 M Cr(NO3)3 and 0.01 M NaF than in the NaF-containing solution. This was caused by the pH-driven deposition of Cr(III) species (>pH 4.5),31 according to the reaction:

\[
\text{Cr}^{3+} + 3\text{OH}^- \rightarrow \text{Cr(OH)}_3^- \tag{2}
\]

Wen et al. revealed that the as-deposited coating formed in a solution of Cr(NO3)3 displayed a porous coating structure after a conversion treatment for 60 s, which played a barrier against the matrix dissolution.34 Notably, the coatings displayed the popular presence of defects and cracks with the evident spallings after a prolonged conversion treatment.8,21 As a consequence, the concentration of H_2O_2 after 5400 s in the stirred solution containing 0.01 M Cr(NO3)3, and 0.01 M NaF was the same as that following a same time of immersion in the H_2SO4 solution containing only NaF. Interestingly, the H_2SO4 solution containing 0.01 M Cr(NO3)3, 0.015 M K2ZrF6 and 0.01 M NaF revealed similar amount of H_2O_2 after immersion for 300, 600, 1200 and 5400 s to those found following immersion in the H_2SO4 solution containing only an addition of 0.015 M K2ZrF6. The similarity suggests that the presence of hexafluorozirconate in the former solution significantly inhibits the aggressiveness of the F− ions. This may be associated with the formation of a dimer [F5Zr-O-ZrF5]− species during hydrolysis of ZrF5− in the H_2O2-containing medium, the F− ions promoted the formation of the hydroperoxyl ions for the peroxide ionization for the dimer compound formation.52 The reaction Equations 3–4 and 5–7 are the H2O2-self-ionization and the

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**Figure 8.** Surface topographies investigated by atomic force microscopy of (a) the sputtering-deposited aluminum and (b) electropolished aluminum; the red arrows in (a) highlight voids in the sputtering-deposited aluminum surface, with a depth of ~20 nm.

**Figure 9.** Plots of H_2O_2 concentrations with dependence on the reaction times during aluminum conversion treatments in the different naturally-aerated solutions.
The high reactivity of aluminum substrate provides the source of free fluoroine-promoted dimer formation process respectively as follows,

\[
ZrF_6^{2-} + H_2O \rightarrow ZrF_5H_2O^+ + F^- (ZrF_6^{2-} \text{hydrolysis process})
\]  

(3)

\[
2ZrF_5 \bullet H_2O^+ + H_2O_2 + 2OH^- \rightarrow [F_2ZrOO-ZrF_5]^4^- + 4H_2O
\]  

(dimer formation process)

(4)

\[
H_2O_2 + F^- \rightarrow HO_2^- + HF (\text{peroxide ionization process})
\]  

(5)

\[
HO_2^- + F^- \rightarrow O_2^{2-} + HF (\text{peroxide ionization process})
\]  

(6)

\[
2ZrF_5 \bullet H_2O^+ + O_2^{2-} \rightarrow [F_2ZrOO-ZrF_5]^4^- + 2H_2O
\]  

(dimer formation process)

(7)

In addition, the chemical exchange between ZrF_6^{2-} and F^- possibly generated the fluoride intermediate ZrF_5^{2-}, which would reduce the concentration of F^- ions in the reaction solution.35,36

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The differing story of the interfacial pH evolution during the conversion coating of aluminum needs the future focus, which also is the control factor for the chromium chemistry.
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