Formation of Chromate Conversion Coatings on Aluminum and Its Alloys

In situ XANES Study

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In situ X-ray adsorption near-edge structure (XANES) has been used to investigate the formation of chromate conversion coatings on pure Al, commercial Al alloys (AA1100, AA2024, and AA7075), and a series of binary Al-Cu alloys. The method employed cells designed to determine the growth of the total chromium [Cr(VI)] and hexavalent chromium [Cr(VI)] in the chromate conversion coating (CCC) as a function of exposure time to a chromate solution. Three sets of data were obtained, where (i) the Al was exposed to only a limited amount of solution; (ii) the chromate solution was excluded after short periods of repeated exposures to the solution; and (iii) the Al was exposed continuously to the chromate solution. All the results showed a very rapid initial growth within the first seconds, followed by a continued increase in thickness for exposures up to 1 h. Measurements with Al-Cu binary alloys demonstrated that the difference observed in AA2024 and AA1100 may not be due to Cu alloying. The proportion of Cr(VI) in the coatings becomes approximately constant after 180 s of exposure for all the specimens examined, even though the coatings continued to grow.

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Considerable efforts have been made in the understanding of the formation and properties of chromate conversion coatings (CCCs) because of the excellent protection afforded by the coating as well as its ease of application. Studies have also been carried out to understand the role of the coating in protecting surfaces as a basis for developing replacements for CCCs because of its toxicity. Very few in situ CCC measurements have been carried out. An example of open-circuit potential measurements is given by Campestrini et al.1 Goeminne et al.2 and Vuillemin et al.3 used electrochemical reduction of chromate on graphite electrodes to monitor chromate that did not react at the Al surface. The former investigators used a rotating ring-disk method with an Al alloy as the disk and graphite ring.4 The latter investigators employed a flow system with a graphite electrode monitoring the growth and dissolution of the films.3-12 X-ray adsorption offers a powerful method for the in situ study of the kinetics of chemical changes taking place at surfaces, by monitoring the growth and dissolution of the films.12-13 X-ray adsorption near-edge structure (XANES) has been used to study the products of reactions of chromate conversion coatings (CCC) adhering to Al surfaces, and the behavior of these products with time and exposure to solutions.4-13 CCCs are made up of Cr(III) and Cr(VI) species such as in CrO42−; the latter is believed to be responsible for CCC’s ability to protect scratches on a metal surface undergoing further electrochemical degradation. A factor that assists in the determination of Cr speciation is a distinct pre-edge peak at 5993 eV in the XANES spectrum when hexavalent chromium Cr(VI) is present. In addition, the ratio of height above the edge arising from all chromium species present [Cr(total)] to the pre-edge height [only Cr(VI)] provides a quantitative measure of Cr(VI) content in the CCC. However, XANES measurements of CCC have generally been made ex situ.

In this study, we introduce designs of cells that allow monitoring of a specimen surface exposed to a chromate solution without being removed from the aqueous environment. We present data on aluminum and its alloys (i) when exposed to a limited volume of solution; (ii) when subjected to repeated exposure to the chromate solution; and (iii) when continuously exposed to the CCC solution. From these findings, we discuss the kinetics of the CCC formation and the effect of Cu additions.

Experimental

One set of specimens used in this study were rectangular pieces of pure Al (99.999% purity), AA1100-O, AA2024-T3, AA7075-T6, and binary high purity Al-Cu solid solution alloys (Cu contents: 0.2, 1, 2, and 4 wt %), cut to dimensions of ca. 12 × 12 × 1 mm.

Table I lists the specifications of composition for the commercial alloys. The binary Al-Cu alloys [Cu(II)] solution annealed at 535°C and quenched in water; the alloys were then aged at 150°C for a period of 24 h. No microstructural analysis of the specimen surfaces was done. The surfaces were wet ground on a 600-grit abrasive paper. The specimens were then immersed in 8 wt % KOH for 5 min, rinsed in distilled water, immersed in 50 wt % HNO3 for 5 min, and finally rinsed thoroughly in distilled water. The samples were then mounted on a plastic support. All specimens were prepared less than 1 h before the measurements. Commercial Alodine 1200 (Parker Amchen, Michigan) was used at a concentration of 7.5 g L−1 and at room temperature.

We developed a novel cell similar in principle to that used by Toney et al.14 in which one side of the specimen is covered with a plastic film transparent to X-rays separated by a thin, ~10 μm thick, liquid layer,15 as schematically shown in Fig. 1. The cell is completely sealed except for a tube connected to a reservoir of a chromate solution. By lifting the reservoir, hydrostatic pressure in the cell is increased so the solution flows into the cell and infiltrates the membrane (Fig. 1a). Suction or lowering the reservoir causes a fall in pressure in the cell, so that the solution is drained off and the membrane drawn up against the specimen surface excluding all but a very thin film of liquid thereby suppressing the surface reaction (Fig. 1b). Expelling the solution was ensured by pressing the membrane against the specimen immediately after deflation. XANES measurements were then made. Using this approach, exposure of the specimen surface to a bulk chromate solution can be interrupted to permit XANES measurements. Repeated exposure-interruption measurement cycles permit detailed characterizations of coating growth to be carried out.

This cell was also used when the chromate solution was not completely drained from the cell, leaving a thin layer of solution trapped in contact with only the specimen surfaces. Trapping the chromate was achieved by having a sample with sharp edges, against which the membrane formed a seal. Changes in the chromium chemistry with increasing exposure time were monitored as the chromate reacted with the Al sample.
The growth of the CCC on the specimen surfaces during continuous exposure to the chromate solution also was monitored in a different cell, somewhat similar to that described previously. Foil of the metal or alloy (ca. 60 μm thick) was mounted over a 15 × 5 mm window cut into one side of a small, rectangular 60 ml plastic tissue culture flask so that one side of the foil could be exposed to the solution. The foils were annealed at 400°C and water quenched after rolling and exposed to 8 wt % KOH for 5 min, rinsed in distilled water, immersed in 50 wt % HNO₃ for 5 min, and finally rinsed thoroughly in distilled water.

The XANES spectra were made on Beamline X-10C at the National Synchrotron Light Source (Brookhaven National Laboratory). The specimen surface was oriented at an angle of 45° to the incident beam, which was approximately 5 × 0.5 mm. A solid-state detector was positioned at 90° to the incident beam to collect fluorescence radiation from the sample or in two sets of experiments, from the sample and chromate solution. The intensity of the fluorescence was normalized relative to the incident beam. Details of similar experimental procedure for the XANES studies are given elsewhere. An X-ray beam energy of 6 keV was used and the composition of the Alodine solution was taken as 30 mM CrO₃, 14.5 mM NaF, 15 mM KBF₄, 2 mM K₂ZrF₆, and 3 mM K₃Fe(CN)₆. Curve A in Fig. 2 shows the predicted Cr fluorescence intensities as a function of solution thickness. The Cr intensity varies linearly with thickness below about 60 μm. Between 60 and 140 μm the incoming and scattered X-rays are absorbed within the solution, and the intensity of the Cr signal increases progressively less rapidly with thickness, eventually reaching a constant value above about 140 μm, an effective infinite solution thickness. If the thickness of solution trapped between the membrane and the substrate was above 140 μm, the Cr signal would decrease as the formation of the CCC extracted chromate from the solution. No signal would be observed from the CCC because of absorption of the X-rays in the solution. With solution thickness above about 60 μm, detectable changes in both the solution and at the specimen surface should be observed.

Figure 3a shows a series of in situ repeated XANES spectra for AA 1100 with trapped chromate solution. An important feature of the results was the presence of an isosbestic point at energy of 6012 eV, indicating that there was no significant change in the amount of Cr detected. If there was absorption by the water the detected signal from the Cr would decrease as the Cr was extracted from the solution trapped between the membrane and the substrate was above 140 μm. The Cr signal would decrease as the formation of the CCC extracted chromate from the solution. No signal would be observed from the CCC because of absorption of the X-rays in the solution. With solution thickness above about 60 μm, detectable changes in both the solution and at the specimen surface should be observed.

Table I. Specifications of composition for commercial Al Alloys (from Ref. 25).

| AA number | Si   | Fe   | Cu   | Mn  | Mg  | Cr  | Zn  | Ti |
|-----------|------|------|------|-----|-----|-----|-----|----|
| 1100      | 1.00 |      |      | 0.05|      | 0.05|     |    |
| 2024      | 0.50 | 0.50 | 3.8–4.9 | 0.30–0.9 | 1.2–1.8 | 0.10 | 0.10 | 0.15 |
| 7075      | 0.40 | 0.50 | 1.2–2.0 | 0.30 | 2.1–2.9 | 0.18–0.28 | 5.1–6.1 | 0.20 |

Reaction with a limited volume of solution.—Measurements were carried out to show that the chromium speciation reached a final state when a limited volume of the chromating solution was trapped between the membrane and an Al surface. In the example given an Al-0.2% Cu sample was used. Continuous XANES measurements were made which monitored the changes in both electrolyte and a CCC formed during exposure. This was achieved by confining the chromating solution between the sample and the plastic membrane to a limited volume. Each XANES scan took about 390 s and was repeated every 78 s. The thickness of the solution layer was too thin to be measured with available techniques, although curvature of the membrane was apparent. If too small a layer of solution was trapped, the conversion of the chromate occurred in less than 78 s and was too rapid to monitor. If thick solution layers were used then the chromate in solution would mask the reactions on the surface and only changes in the solution would be seen. Calculations of the effects of solution thickness were therefore carried out.

The energy dispersive X-ray fluorescence intensity of chromium as a function of the thickness of a layer of solution was calculated based on the composition of the chromating solution employing a computer program, NRLXRF. The program uses a fundamental parameters method that takes into account the energy of the beam and the effects of absorption due to filters and multielement samples. An X-ray beam energy of 6 keV was used and the composition of the Alodine solution was taken as 30 mM CrO₃, 14.5 mM NaF, 15 mM KBF₄, 2 mM K₂ZrF₆, and 3 mM K₃Fe(CN)₆. Calculations showed that the absorption was dominated by the oxygen in the water rather than the chromium or heavier elements in the solution.

Figure 1. Schematic of the cell used for the in situ study of the formation of chromate conversion coatings. The cell is shown (a) with a covering membrane inflated to allow contact with the bulk chromate solution, and (b) with the membrane deflated displacing the solution and pressing in close contact with the specimen surface.

The in situ investigation of the CCC formation kinetics is described in three parts. First, we describe the reactions taking place with a limited but measurable amount of chromate solution to determine the kinetics of reaction and any subsequent chemical changes once the chromate in solution had reacted to form a conversion coating. Measurements were then made repeatedly exposing Al surfaces to the bulk chromate solution for brief periods of time, followed by excluding the chromate solution from contact with the Al, leaving a very thin layer of reacted solution between the surface and the plastic membrane. Finally, the growth of a CCC was monitored while it remained in contact with bulk chromate solution, to ensure that any significant aging of the surface did not dramatically change the growth kinetics when the chromate solution was excluded during the XANES measurements.

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tion and incorporated into the CCC. The data in Fig. 3a are therefore consistent with the formation of a stable CCC by reactions that fully extract chromate from the small volume of trapped solution. At the end of the reaction the fraction of Cr(VI) ions was ca. 33%.

The results in Fig. 3a can be modeled by taking relative proportions of the spectra for the chromating solution as represented by the first spectrum recorded, and the spectrum for the CCC, represented by the spectra after 390 s. Figure 3b presents the modeled results. The figure caption gives the ratios of those of the solution and the CCC used in the calculation. The growth of the CCC derived from the modeling is shown in Fig. 4, which demonstrates that the CCC formed in a restricted volume of solution is compositionally stable once the formation reaction is complete. In these experiments, the initial fraction of Cr(VI) within the CCC was masked by chromate in solution, which dominated the observed spectra at short exposure times. This was not the case when the plastic film was completely deflated and minimal solution was trapped between the film and the sample, as is described below for repetitive exposures of the sample to bulk chromating solution.

Interrupted exposures to chromating solution.—Using the cell illustrated in Fig. 1, we were able to grow a CCC in steps using the exposure-interruption-measurement approach described in the Experimental section. The time of exposure to the chromate solution ranged from 2 to 300 s to enable monitoring of rapid initial changes in the CCC, as well as the relatively slower subsequent exposures. Figure 5a presents a series of in situ XANES spectra of the stepwise growth of the CCC film on AA 2024-T3. After each exposure period, the surface reaction was suppressed by deflating the membrane and expelling the solution from the region between the sample and the plastic film. The height of the pre-edge peak seen (at 5993 eV) was a measure of the amount of Cr(VI) ions present in the CCC, while that above the absorption edge represents the total amount of all Cr species. The height above the edge was not well defined, nor were measurements made well above the edge to better define the height as is normally done, because the time during the measurements was kept to a minimum. The analysis of Fig. 3 showed that the two major Cr-containing constituents, the chromating solution and in particular that of the CCC, could be quantified at the isosbestic point. Hence, the total amount of Cr could be measured by the height at the isosbestic point and correcting it to the edge height. This approach required that there be only two types of Cr species in the film. The isosbestic point occurs at a higher energy of 6026 eV rather than 6012 eV for solutions of Cr(III) and Cr(VI),13 indicating the Cr(III) in the CCC has a different near-edge structure, which may change with time as the Cr(III) surface films are not normally stable, well-structured compounds.5-7,9-13 The low integration time of 1 s for each point and the low amount of Cr in the CCC also increased the scatter in the XANES data. This reduced the accuracy with which the height of the pre-edge Cr(VI) peak could be determined. In view of the low signal-to-noise ratio, the greatest uncertainty in the relative Cr(VI) content exists for data collected in the first few exposures. With increasing thickness of the CCC, the signal-to-noise ratio improved, and the uncertainty associated with the relative Cr(VI) content determination was reduced. These factors lead to a reduced confidence in the estimation of the fraction of Cr(VI) of about ±20% in an effort to monitor the in situ kinetics of growth of the CCC. Nonetheless, the trends in the behavior with time are clear, even though the absolute values may be uncertain. Ex situ XANES determinations of the Cr ratio have been reported and offer more accurate measures of the Cr(VI) ratios.5,6,13 The scatter in the results is seen in Fig. 5b to be very high at the start, but after 20 s of total repeated exposures to the bulk solution, the trends in the growth behavior of the CCC and Cr(VI) are clearly distinguishable, as is the decrease in the Cr(VI) content with increasing CCC thickness. Repeated scans while the plastic film was deflated showed reproducibility, within the scatter of the results, indicating that the reactions were complete during the first scan, no compositional changes took place due to solution reaction or aging of the CCC, and there was no leakage of solution into the region between the sample and the membrane. These findings are consistent with the results in Fig. 5b.
Commercial CCC bath formulations to accelerate the coating deposition rate on Mg-containing intermetallics slowed with increasing exposure time. The cyanide is derived from potassium ferricyanide that is added to the bath to increase Cu content due to adsorption of cyanide on the Cu-rich sites. McGovern et al. concluded that the deposition rate on Mg-containing intermetallics slowed with increasing exposure time. The rates for AA2024-T3 decline with the buildup of the CCC layer, following a rate with time raised to a power distinctly smaller than one-half found by other investigators. A similar behavior to AA2024-T3, with a very rapid decrease with immersion time, indicating continuous growth of the CCC layer during all consecutive exposures. The results of these repeated exposures tests using a membrane cell are shown in Fig. 7a and b. The CCC formation behavior on the Al–Cu binary alloys differed from that on the commercial alloys in several ways. Based on the variation in total Cr as a function of immersion time, CCC formation rate showed a plateau after an initial episode of rapid growth. The length of the plateau increased with Cu content from 140 to 180 s. After the plateau, rates again decreased from close to 60% to about 40% after 100 s. The proportion of Cr(VI) in the CCC becomes constant after 180 s, even though the CCC continued to grow.

Figure 6 presents the changes in the amounts of Cr(VI), Cr(total), and the ratio of Cr(VI)/Cr(total) in a CCC formed on AA1100 up to an exposure time of 600 s. The Cr(VI) fraction in the CCC showed similar behavior to AA2024-T3, with a very rapid decrease with time as the CCC thickened. The amounts of Cr(VI) and Cr(total) again showed the very rapid initial growth rate, but continued to increase with time at a steady rate compared with that of the AA 2024-T3 (Fig. 5), where the rate continued to decrease. Linear in situ growth of a chromate-phosphate film on a 99.5% Al surface in a 0.03 M CrO$_3$ solution containing ~50 mM HF has been observed using a ring electrode, but the growth behavior varied with fluoride contents. Ex situ Auger analysis with a similar alloy and solutions but static conditions also showed a linear behavior.

Measurements were also carried out on AA 7075, but the chromium in the alloy dominated the measurements and prevented a detailed analysis of the CCC.

The initial rapid growth of the CCC has been attributed to the role of cathodic sites on the surface generally due to alloying element-rich intermetallic particles, which have been identified as sites that nucleate the CCC. McGovern et al. concluded that the deposition rate on Mg-containing intermetallics slowed with increased Cu content due to adsorption of cyanide on the Cu-rich sites. The cyanide is derived from potassium ferricyanide that is added to commercial CCC bath formulations to accelerate the coating deposition process on aluminum. However, McGovern’s findings suggest an unintended consequence on CCC formation for Cr-containing Al alloys. These explanations offer a possible cause for the marked decrease in CCC deposition rate on AA2024-T3 compared to AA1100. If significant differences were caused by cathodic sites associated with Cu in the alloy, differences should be seen with Al–Cu binary alloys containing 0.2 to 4% Cu. The results of these repeated exposures tests using a membrane cell are shown in Fig. 7a and b. The CCC formation behavior on the Al–Cu binary alloys differed from that on the commercial alloys in several ways. Based on the variation in total Cr as a function of immersion time, CCC formation rate showed a plateau after an initial episode of rapid growth. The length of the plateau increased with Cu content from 140 to 180 s for 0.2 and 4.0% Cu, respectively. Pure Al showed only an indication of a plateau up to around 20 s. After the plateau, rates again
increased, being approximately constant up to 600 s. The ratios of Cr(VI)/H2O49 to Cr(total) in CCCs formed on the Al–Cu binary alloys showed less variation with coating time than the commercial alloys, as shown by a set of measurements in Fig. 8. Hence, other than the delay after the initial deposition of the CCC, the additions of Cu did not show any trends. The major difference in growth behavior was shown by AA2024-T3. One possible cause is the greater concentration of Cu-rich second-phase particles in this alloy, and the role of these particles in the growth of the CCC requires further study.

**Continuous exposures in contact with chromate solution.**—The experiments with the repeated exposures in the membrane cell indicated that the thickness of the CCC would increase continually with time, the possible exception to this being AA2024-T3, where the growth rates at longer immersion times decreased nearly to zero. Ex situ measurements by Kendig et al.12 found that the CCC thickness reached a constant value after about 5 min immersion. These samples were washed and dried following a timed exposure in chromate solution. A similar behavior was seen by Katzman et al.23 for AA1100. One possible cause for the difference in the growth behavior in our result where the film continues to grow may be related to aging of the coating when the bulk chromate solution was excluded. Alternatively, the adherence of the film may change and even though the film continued to grow, the outer layers of the film may wash off upon rinsing in water, leaving an adherent inner layer. Measurements were therefore carried out to monitor the in situ growth of the CCC without restricting the access to the chromate solution, and to remove any possible effects of aging.

The measurements were made using a thin, 60 μm alloy foil window covering a cutout in a plastic container holding the chromate solution. The X-rays penetrated through the foil, then through the CCC building up on the foil, and into the chromate solution. Because of the geometry and the Cr(VI) in solution, a quantitative analysis of the Cr speciation in the CCC was not attempted. Nonetheless, qualitative indications of the growth of the CCC were possible.

In situ XANES spectra for a continuously growing CCC are shown in Fig. 9a for an Al-0.2% Cu foil. The spectra were measured every 225 s for an hour starting after a 30 s exposure to the solution. In Fig. 9a, the spectrum with the lowest intensity, depicted by white circles, corresponds to the first scan. Also shown are the consecutive measurements.

**Figure 7.** Variations in the intensity of Cr(VI), total Cr, and the Cr(VI) fraction with time of exposure to bulk chromate solution for (a) Al-0.2% Cu, and (b) Al-4% Cu.

**Figure 8.** Variations in the intensity of the Cr(VI) fraction with time of exposure to bulk chromate solution for Al–Cu alloys.

**Figure 9.** (a) XANES acquired during formation of a conversion coating on Al-0.2% Cu foil continuously exposed to the chromate solution. Timing was started upon adding the chromate solution. Times on each curve indicate when the scans were started. (b) Variations in intensity of the chromate Cr(VI), the total Cr, and the Cr(VI) fraction with time.
spectra measured every 450 s, which show an increase of intensity with increasing immersion time. Figure 9b shows the changes in the intensity of Cr(total) and Cr(VI). The first XANES scan indicated that the major fraction of the Cr(total) was due to Cr(VI) from the chromate solution. As the CCC grew, the total Cr increased and the fraction of Cr(VI) recorded decreased to levels observed using the other methods of monitoring CCC deposits after about 3000 s. The growth rate appeared linear on the first 500 s and decreased by a factor of about 2 toward the end of the test.

The film did not reach a constant thickness after 5 min, but continued to increase for the 60 min period of the measurement and excluded any dramatic aging effects during the experiments where the sample was repeatedly exposed to bulk chromate that enabled the film to grow continuously. Nevertheless, minor effects resulting from the exclusion of the chromate solution cannot be ruled out. Changes in the nature of the film and the growth processes of the thick CCC are probably responsible for the lack of adherence and the loss of the outer part of the film on rinsing. The object of the present study, to demonstrate the application of the AI foil technique to study the growth of conversion layers, was achieved, but further work should also be carried out with AA2024-T3 as this alloy did show changes indicative of comparatively limited CCC formation.

The NRLXRF calculation of the expected fluorescence emanating from the chromate solution and the CCC as a function of its thickness for the foil geometry are included in Fig. 2. An atomic ratio of Cr to O in the CCC of 3 with a density of 2.5 g/cm$^3$ was used in the calculations. Three curves relate to this calculation. The Cr fluorescence from the CCC, the solution, and the sum of these two intensities which represent the detected signal. The unity slope in logarithmic plot for the CCC alone shows that the Cr fluorescence signal increases in proportion to its thickness up to 7 μm. At greater thicknesses the self-absorption within the CCC slows the increase and an infinite thickness is reached above about 30 μm. The Cr signal only from the solution remains constant up to a CCC thickness of 7 μm, virtually unaffected by X-ray absorption by the CCC. Above this thickness the signal rapidly decreases because of the absorption in the CCC. The summed fluorescence curve shows that the solution only dominates until a CCC thickness of 0.01 μm is reached. Between 0.01 and 1 μm both the solution and the CCC contribute, whereas above 2 μm the CCC fluorescence dominates.

The calculated intensities emitted in Fig. 2 may be used as a template to estimate the possible thickness range of the deposit. Two critical thicknesses of the CCC are indicated in Fig. 2. The first is around 0.01 μm, when the CCC begins to contribute to the predicted Cr intensity. For a very thin CCC the intensity is dominated by emission from the Cr in solution and would be 100% Cr(VI). From the start of the experiment both the total Cr increased and the fraction of Cr(VI) decreased, demonstrating (based on the calculations in Fig. 2) that the CCC grew to a thickness greater than 0.01 μm within the first 30 s. Had the CCC thickness been smaller, the chromate solution could have been used as a standard. The second critical change takes place when the CCC thickness is greater than 10 μm, when the intensity no longer increases with increasing CCC thickness. The continued increase in the total Cr with time in Fig. 9b indicates that this stage had not been reached. The fraction of Cr(VI) approached a value of around 40%, close to that observed for the other in situ measurements, indicating that the CCC was dominating the observed fluorescence intensity. From Fig. 2, this occurs at a thickness of 1 μm indicating the film was less than this thickness at the end of the exposure time. Generally, the thickness quoted for the CCC is in the range of a few tens of nanometers. $^{23,24}$ Katzen et al. give values of 70 nm on AA1100, which remained constant for 4 to 16 min. $^{23}$ The difference between these and the results in Fig. 9 where the CCC continued to grow strongly suggests that the CCC is composed of an inner and outer layer that can be removed on rinsing.

**Conclusion**

Three techniques have been explored to demonstrate the in situ formation of chromate conversion coatings on pure Al using X-ray absorption spectroscopy. Novel cells were used to observe the growth on commercial Al alloys (AA2024-T3, AA1100, and AA7075-T6), and a series of binary solid solution Al–Cu alloys by in situ XANES measurements using a new type of electrochemical cell. The techniques employed allowed the determination of hexavalent chromium ([Cr(VI)]) and total chromium ([Cr(total)]) in conversion coatings as a function of exposure time to a chromate solution. All measurements showed an extremely rapid initial growth of the conversion coating. With Cu–Al alloys there was a delay in the growth, followed by approximately linear kinetics. Extended time measurements were carried out on an Al-0.2% Cu, which demonstrated that the conversion coating continued to grow for 1 h. A distinctly decreasing rate of growth was observed with Al2024, and an approximately linear growth was apparent for AA1100 after the rapid initial behavior. The growth kinetics of AA1100 and AA2024 could not be directly attributed to Cu alloying alone, as shown by the Al–Cu alloy results, suggesting that microstructural heterogeneity may play an important role in establishing overall CCC growth kinetics. Measurements on AA7075-T6 were unsuccessful because the Cr in alloy dominated the Cr measurements. For all specimens the proportion of Cr(VI) in the coatings becomes approximately constant after 180 s of exposure time as the coatings continue to grow.

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