Surface enhanced Raman scattering (SERS) was used to observe interactions of dilute CrVI solutions with silver and copper surfaces in situ. Using silver as a model surface which supports strong SERS with a 514.5 nm laser, it was possible to observe CrVI at the near monolayer level, and the spectra were compared to those from CrIII oxyhydroxide species and CrIII/CrVI mixed oxide.

Similar experiments were conducted with Cu surfaces and 785 nm excitation. Upon exposure to CrVI solution, the characteristic Cu oxide Raman bands disappeared, and a CrVI band increased in intensity over a period of ~20 h. The intensity of the CrVI band on Cu became self-limiting after the formation of several CrII monolayers, as supported by chronoamperometry experiments. This CrVI spectrum was stable after CrIII was removed from the solution provided the potential remained negative of ~200 mV vs. Ag/AgCl. The results support the conclusion that CrIII is reductively adsorbed to Cu at the near neutral pH and open circuit potentials expected for Cu/Al alloys in field applications. The CrIII film is stable and is a strong inhibitor of electron transfer in general and oxygen reduction in particular. An important mechanistic feature of CrIII formation is the substitution lability of CrIII compared to CrII. The CrIII-O bond can be broken much more rapidly than the substitution inert CrII-O bond, making formation of CrII/III mixed oxide kinetically favorable. Once reduced to CrIII, however, the substitution inert oxyhydroxide film is much less labile. An important and central feature of CrIII as a corrosion inhibitor is its transformation via reductive adsorption from a mobile, substitution labile CrIII form to an insoluble, substitution inert CrII oxyhydroxide. Furthermore, CrIII reduction is likely to occur at cathodic sites previously responsible for oxygen reduction, which are then permanently blocked by a stable CrII film with a thickness of a few monolayers.

Currently, chromate conversion coatings (CCCs), and chromate-based barrier coatings and paints are preferred for the treatment of aluminum alloys because they provide both excellent adhesion properties and corrosion inhibition. Routinely applied on these alloys, however, are a large source of environmentally hazardous waste containing the hexavalent chromium present in these coatings. Hexavalent chromium is a danger to worker health and its use and disposal is limited or prohibited by various local, state, and federal regulations. In the search for suitable nonchromate replacements, a basic understanding of the mechanism by which chromate-based protection systems provide such excellent protection will be invaluable.

Considerable research has centered on the use of chromate conversion coatings on aluminum aircraft alloy AA-2024 T3 which contains, by weight, 3.8-4.9% copper, 1.2-1.8% magnesium, and less than 1% each of other trace metals, the balance being aluminum. All of the AA-2XXX series alloys are prone to corrosion, particularly pitting and stress corrosion cracking, arising from the inhomogeneous distribution of copper in these alloys. This distribution leads to the establishment of local galvanic cells between copper-rich and copper-poor areas and thus destructive localized corrosion. Approximately 60% of the secondary phase intermetallic particles found in AA-2024 T3 are copper-rich Al2CuMg. CCCs such as commercially available Alodine 1200 form a corrosion-inhibiting film on both the matrix and the intermetallics of AA-2024 T3. The mechanism by which a CCC film protects AA-2024 T3, however, is not fully understood. In an attempt to better understand the relationship between CCCs and copper-rich intermetallics, previous studies in this laboratory were undertaken with pure copper exposed to CrVI in solution. These studies indicate that CrVI inhibits the cathodic activity of copper in aluminum alloys, particularly toward oxygen reduction.

The current approach uses Raman spectroscopy, specifically surface enhanced Raman scattering (SERS), to investigate the formation of CrIII oxyhydroxide on pure copper. Unlike many surface techniques, Raman spectroscopy probes molecular structure in addition to speciation. Additionally, it is nondestructive and in situ analysis is straightforward, providing a means to acquire spectra under potential control. Spectral enhancement factors of greater than 106 are obtainable with SERS on silver, gold, and copper. Because of the SERS enhancement, the molecular structure of even a monolayer of a Raman active species on roughened copper can be probed. In fact, it is the scattering of molecules on the first layer of a surface that receives the greatest enhancement. The effect diminishes significantly with increasing distance from the surface. Therefore, not only is the immediate surface spectrum enhanced, but interference from species not on the immediate surface is minimized.

Silver was initially used as a model in this study to better understand the formation of a CrIII oxyhydroxide and/or a CrIII/CrVI mixed oxide from CrVI in solution. Subsequent experiments were then performed on copper. Previous work in this laboratory provided Coulombic evidence of the formation of a near-monolayer CrIII film on copper exposed to solution CrVI. This work provides an in situ spectroscopic probe of the formation and structure of this film.

**Experimental**

**Materials.—**All chemicals were reagent grade and were used as received. Potassium sulfate, potassium hydroxide, and sodium hydroxide were obtained from Mallinckrodt; potassium dichromate and chromium(III) nitrate from Alfa Aesar; cupric sulfate, anhydrous powder from J. T. Baker; silver nitrate from Fisher Scientific; and chromium potassium sulfate (chrome alum) from Allied Chemical. All solutions were prepared and rinsing was performed with Barnstead Nanopure water, 17.8 MΩ minimum resistivity. The silver substrate was 99.9985% silver foil, 0.1 mm thick, obtained from Johnson Matthey Materials Technology. Unless otherwise noted, the copper substrate was 99.99% copper sheet, 1.0 mm thick, obtained from Goodfellow. AA-2024 T3 sheet, 0.025 in (0.064 mm) thick, was obtained from Alcoa.

Various chromium compounds were prepared using the methods described by Xia et al. Ag2CrO4 was prepared by dissolving 0.4 g K2Cr2O7 in 50 mL H2O and then adding 1.3 g AgNO3. The precipitate, Ag2CrO4, formed immediately and was filtered, rinsed with H2O, and air dried. Cr(OH)3 was prepared by dissolving 4.0 g Cr(NO3)3·9H2O in 25 mL H2O; 1 M KOH was added dropwise to the stirred solution until the pH reached 4.5. The precipitate,
Cr(OH)$_3$ was filtered, rinsed with H$_2$O, and air dried. The Cr(VI)/Cr$^{3+}$ mixed oxide was prepared by dissolving 4.0 g Cr(NO$_3$)$_3$·9H$_2$O and 0.5 g K$_2$Cr$_2$O$_7$ in 50 mL H$_2$O. 1.0 M NaOH was added dropwise to the stirred solution until the pH exceeded 4.5. The mixed oxide precipitate was filtered, rinsed with H$_2$O, and air dried. Concentrated Cr$^{3+}$ solutions added to electrochemical cells were prepared with K$_2$Cr$_2$O$_7$ and H$_2$O.

**Instrumentation.**—In all cases the reference electrode was Ag/AgCl (Bioanalytical Systems) and the auxiliary electrode was a platinum wire. All noted potential values are vs. Ag/AgCl. Oxidation/reduction cycles (ORCs) for roughening of the silver foil electrode and the copper rod were performed with a Bioanalytical Systems 100B electrochemical workstation. Copper sheet deposition roughening and chronoamperometry were performed with a Gamry PC3/300 potentiostat. All in situ potentiostatic control was performed with a Bioanalytical Systems model PWR-3 potentiostat.

Raman spectra on the silver substrate were acquired with a 514.5 nm laser on an FT.1.5 Kaiser spectrophotograph with a holographic grating, 180° backscattered geometry with a laser spot size of $\sim$50 $\mu$m. A video charge coupled device (CCD) camera was used to focus the laser at low power ($\sim$200 $\mu$W) on the silver foil. Spectra were acquired with 5 mW of laser power at the sample and were not intensity corrected for instrumental response. Raman spectra of the copper sheet substrate were acquired with a 785 nm laser with a Chromex Raman 2000 spectrophotograph equipped with a 600 line/mm grating optimized at 1000 nm and an Olympus 40 times magnification/0.80 W immersible objective giving a spot size of $\sim$3-4 $\mu$m with 10 mW of laser power provided at the sample. A Logitech QuickCam was used for focusing. Raman spectra of the copper rod substrate were acquired with macro optics consisting of a gold coated, off-axis paraboloidal reflector installed in the same Chromex Raman 2000 spectrophotograph with 785 nm excitation. The laser spot size was $\sim$50 $\mu$m with 50 mW of laser power provided at the sample. Focal position was determined by maximizing the intensity of the Cu$_2$O bands discussed below. All spectra acquired with the Chromex Raman 2000 were intensity corrected using National Institute of Standards and Technology standard SRM2241 and the method described by Ray et al.13 Both the Kaiser and the Chromex spectrophotographs were equipped with liquid nitrogen cooled CCD detectors cooled to $-110$ and $-90^\circ$C, respectively. Integration times for all spectra were 30 s or less.

X-ray photoelectric spectroscopy was performed with a VG Scientific Escalab MKII system with a Mg K$_\alpha$ source and a range of 0 to 1000 eV binding energy. An Orion model 520 A pH meter was used to determine pH values. Absorbance spectra of aliquots of Cr$^{3+}$ solutions from the various electrochemical cells were acquired with a Perkin-Elmer Lambda 900 UV/Vis spectrophotometer. Concentrations were determined using the Xia et al. previously determined molar absorptivity of $\varepsilon_{\text{350nm}} = 1.49 \times 10^5$ M$^{-1}$ cm$^{-1}$.12

Sample preparation and spectral acquisition.—**Reference spectra.**—Raman spectra of solid Ag$_2$Cr$_2$O$_7$, solid Cr(OH)$_3$, and solid synthetic Cr$^{3+}$/Cr$^{3+}$ mixed oxide were acquired with 514.5 nm light on the Kaiser spectrophotometer noted above. Solid Cr$_2$O$_3$ was mixed with 100 mM K$_2$SO$_4$ to make a paste before spectral acquisition with the same spectrometer. A Raman spectrum of solid chrome alum (not shown) was acquired with the Chromex spectrophotometer noted above.

**Silver substrate.**—**SERS** requires that the surface of the substrate be roughened in order to promote enhancement. To this end, the silver foil was cut to a strip approximately 0.9 $\times$ 9.0 cm, abraded with successive grits of silicon carbide papers (Buehler P240, P4000) and wetted with Nanopure water and rinsed. The OSC used to roughen the foil was adapted from the procedure of Weaver et al. and consisted of a scan from $-400$ to $+600$ mV, a hold at $+600$ mV for 1 s, a scan from $+600$ to $-400$ mV and then a hold at $-400$ mV for 10 s. The scan rate was 100 mV/s. This cycle was repeated 20 times in 5 mL of 100 mM potassium sulfate. Approximately 1 cm$^2$ of the silver foil was submerged in the electrolyte during roughening. Upon completion of the OSC roughening, the cell was disconnected from the workstation, but the electrodes were left in the OSC solution. The cell was properly positioned in the Raman spectrometer and connected to the potentiostat. The electrochemical cell employed was a $1 \times 5 \times 5$ cm quartz cuvette and all spectra were acquired through a $5 \times 5$ cm face.

**Copper substrate.**—The copper sheet was cut into a 1 cm$^2$ piece and a copper wire was attached to one side with silver epoxy resin (SPI Supplies/Structure Probe, Inc.). The assembly was then embedded in epoxy (Buehler) leaving the smooth side exposed. This copper electrode was hand-polished with successive grits of silicon carbide papers wetted with Nanopure water (Buehler 240, 400, 600, P2400, P4000) and then rinsed in H$_2$O. Electrochemical copper deposition was used to roughen the surface, which promotes the SERS effect. Using a method adapted from Kudelski et al., deposition was accomplished by suspending the electrode face down in an unstirred solution of 500 mM cupric sulfate and holding it at a potential of $-100$ mV for 45 min.13 Immediately after deposition all three electrodes were rinsed and placed in a crystallizing dish (80 mm diam, 40 mm height) which served as the electrochemical cell. The electrolyte was 100 mM potassium sulfate. The copper electrode was arranged with its surface facing up and spectra were acquired through the solution covering the electrode with an immersible objective.

In experiments employing a copper rod as the electrode, the end of the rod was cut at a 45° angle and the rod was enclosed in Teflon shrink tubing (Small Parts Inc.) leaving the beveled face exposed. This beveled face was hand-polished with successive grits of silicon carbide papers (Buehler 240, 400, 600, P2400, P4000) wetted with Nanopure water and then rinsed. Using a method adapted from Weaver et al., roughening was performed with ORCs consisting of a scan from $-1000$ to $+400$ mV, a hold at $+400$ mV for 1 s, a scan from $+400$ to $-1000$ mV and then a hold at $-1000$ mV for 10 s. The scan rate was 100 mV/s. This cycle was repeated 20 times in 10 mL of 100 mM potassium sulfate in a $1 \times 5 \times 5$ cm quartz cell. The cell was disconnected from the workstation with the electrodes remaining in the OSC solution, positioned in the Raman spectrometer and connected to the potentiostat. Spectra were acquired through a $5 \times 5$ cm face with the rod’s beveled face at a 45° angle to the cell face.

**Results and Discussion**

**In situ SERS of silver exposed to chromate.**—As a result of the SERS effect, spectroscopic detection of a monolayer or even a submonolayer of a Raman active species on silver is not uncommon. Silver was, therefore, used first as a model to obtain in situ Raman spectra of a metal exposed to Cr$^{3+}$ in solution. Figure 1 shows four overlaid, in situ spectra of the surface of the silver substrate in the electrochemical cell at $t = 0$ (in K$_2$SO$_4$ solution immediately before addition of Cr$^{3+}$) and at $t = 2$, 10, and 30 min after 100 mM Cr$^{3+}$ solution was added to the cell for a final concentration of 5.6 mM Cr$^{3+}$. Baselines on the spectra have not been adjusted or offset. During acquisition of these spectra no potential was applied, thus allowing the silver foil to remain at its open circuit potential ($OCP$) and thus not shown. The first obvious changes in the spectrum acquired 2 min after the addition of Cr$^{3+}$ are a small feature in the region between 530 and 670 cm$^{-1}$ and a more prominent band between 730 and 890 cm$^{-1}$. With time, both bands in these regions grow. After about 10 min, the higher energy band began to decrease in size and the lower energy band continued to grow. Within 15 min (not shown) the lower energy band clearly dominated the spectrum. The spectrum showed little change between 15 and 30 min. The specific identities of the species giving rise to these two bands are not easily assigned, but previous work with metal surfaces (including silver) exposed to chromate, along with the experimental
conditions, leads to the assumption that they are some type of chromium surface species.\textsuperscript{4,6,9,15} X-ray photoelectron spectroscopy (XPS) analysis of the surface of silver foil subjected to identical treatment showed carbon, oxygen, silver, sulfur, and chromium at atomic percentages of 1.00:0.37:0.22:0.03:0.02, respectively. Specification of chromium with XPS analysis, however, is unreliable as photoreduction of Cr\textsuperscript{VI} to Cr\textsuperscript{III} has been observed.\textsuperscript{16,17} Furthermore, two details indicate that these bands originated from surface and not solution species. Both dichromate and bichromate were present in 5.6 mM Cr\textsuperscript{VI} at the cell pH of ~5 and these species produce a strong sharp band at ~900 cm\textsuperscript{-1}.\textsuperscript{18} Slight defocusing of the laser spot while acquiring the spectra of Fig. 1 caused appearance of a sharp 900 cm\textsuperscript{-1} peak on top of the broad surface scattering. The absence of the 900 cm\textsuperscript{-1} peak with proper focus indicates that the majority of the scattering was collected from the surface rather than the solution. Additionally, when the silver electrode was removed from the cell, rinsed and allowed to dry in room air, the same two bands (slightly shifted, but still strong) were present in spectra acquired of the dry electrode. The shift in peak frequencies of these bands is likely due to changes in hydration of Cr\textsuperscript{III}, and accompanying changes in the relative abundance of water and hydroxide coordination. Assuming these two broad bands are attributable to chromium surface species, comparison to the reference spectra in Fig. 2 implies that the lower energy band arose from a Cr\textsuperscript{III} species and the higher energy band arose from a Cr\textsuperscript{VI} species. The reference spectrum from Maslar et al. of a corroded chromium coupon especially shows the broad nature of a Cr\textsuperscript{III} oxyhydroxide band.\textsuperscript{19} Maslar et al. acquired both Raman spectra and X-ray diffraction (XRD) patterns of the same corroded chromium coupon. The XRD patterns were identified through comparison to the JCPDS International Center for Diffraction Data. By combining the XRD data with the Raman data they attributed the broad band between 535 and 665 cm\textsuperscript{-1} in Fig. 2 to a Cr\textsuperscript{III} species with significant contributions from $\alpha$-CrOOH. Oblonsky et al. also acquired SERS spectra of passive films formed on chromium samples.\textsuperscript{20} These spectra contained a broad band centered at 600 cm\textsuperscript{-1} which was tentatively attributed to Cr(OH)$_2$, CrOOH or a species with no bulk analog. Likewise, the Melendres et al. SERS spectra of chromium samples corroded in NaCl exhibit a broad band centered at ~580-590 cm\textsuperscript{-1}.\textsuperscript{21} Furthermore, both the Maslar et al. work and previous work in this lab have attributed bands in the region from 750 to 950 cm\textsuperscript{-1} to Cr\textsuperscript{III}-O stretches, as can be seen in the spectrum of Cr\textsuperscript{III}/Cr\textsuperscript{VI} mixed oxide in Fig. 2.\textsuperscript{9,22} It should be noted that the cross section of Cr\textsuperscript{VI}-O scattering is generally much larger than that of Cr\textsuperscript{III} oxyhydroxide vibrations and, therefore, the area of the bands is not a direct indicator for quantitative comparison.\textsuperscript{19} Furthermore, the amorphous nature of Cr\textsuperscript{III} films, the degree and type of hydration, and the specific placement and amount of Cr\textsuperscript{VI} within these films all contribute to their broadening and slight variations in Raman shift.\textsuperscript{9,19,20} The distribution of components and band profiles of both the 400-600 and the 700-900 cm\textsuperscript{-1} bands are likely to depend on sample history, pH, and composition.

Finally, as further evidence that these two bands originate from Cr\textsuperscript{III} and Cr\textsuperscript{VI} species, the cell was flushed to obtain a Cr\textsuperscript{VI} concentration of <60 $\mu$M. The spectrum of the electrode in the flushed cell was virtually identical to that at $t = 30$ min in Fig. 1. Upon the application of a potential of ~1000 mV, however, the higher energy band (attributed to Cr\textsuperscript{VI}) nearly disappeared and the lower energy band (attributed to Cr\textsuperscript{III}) broadened, increased slightly in area, and shifted downward about 20 cm\textsuperscript{-1}. An electrochemical experiment was conducted with silver foil in all ways identical to the above Raman experiment with the following exception. After roughening, rather than positioning the cell in the spectrometer, a chronocampometry experiment was performed with the foil held at +177 mV (the approximate OCP of the silver foil prior to the Cr\textsuperscript{VI} injection during the Raman experiment). Using the Clark et al. estimate that the three-electron reduction of Cr\textsuperscript{VI} to form a Cr\textsuperscript{III} monolayer re-
Copper ions contribute approximately 4% of the AA-2024 T3, with the copper-rich intermetallics providing undesirable cathodic sites to drive the oxidative dissolution of the aluminum matrix. Previous work in this laboratory concluded that chromium inhibits cathodic reactions on copper surfaces, particularly oxygen reduction. It was theorized that the reduction of CrVI forms a film of CrIV on the surface which occupies oxygen adsorption sites and acts as a barrier to electron transfer. Figure 3 shows the overlaid, in situ Raman spectroscopic progression of the formation of a chromate containing film on a copper electrode held at a potential of -200 mV, the approximate measured OCP of AA-2024 T3 in 100 mM K2SO4. Again, the spectra were not baseline corrected and share the same intensity scale. At t = 0 (in K2SO4 before addition of CrVI), the spectrum is identical to the roughened copper at its OCP in 100 mM K2SO4. A separate experiment was conducted in a manner identical to the experiment represented in Fig. 3, producing similar spectra. At the conclusion of the experiment, the electrode was removed from the cell, rinsed, and dried in room air. A spectrum of the dried electrode still showed the band attributed to CrIV although it had broadened slightly and was unsymmetric with a maximum intensity at 573 cm⁻¹ and a broad shoulder at 575 cm⁻¹. The band centered at 533 cm⁻¹ suggests an increase in Cr(OH)3 character as shown in the reference spectra of Cr(OH)3 (Fig. 2) which has a broad band centered at 529 cm⁻¹. An increase in Cr(OH)3 character is supported by Sunseri et al., who conducted photocurrent spectroscopic analysis of passive films on chromium and attributed the different compositions in these films to CrIII oxides in various states of hydration. As in the Maslar et al. work, the Sunseri et al. analysis differs from the present work in that the CrIII oxyhydroxide was formed from the oxidation of chromium rather than the reduction of CrVI. In general, however, their work concluded that increasing pH or decreasing potential leads to a more hydrated CrIV species on the surface. If a species similar to CrOOH is indeed predominant on the electrode before rinsing, then removing the electrode from the slightly acidic cell (pH ~ 5) and rinsing with water would subject it to an increased pH and, therefore, lead to an increase of Cr(OH)3 character.

One notable difference between the silver substrate spectra and the copper substrate spectra is the absence of any definite CrIV band in the copper data. In situ SERS spectra were also acquired in two separate experiments with a roughened copper rod substrate in which the rod was first held at -1000 mV in 100 mM K2SO4 for several minutes, potential control was removed, and 800 mM CrVI was added to the cell for a final concentration of ~40 mM CrVI. In both these experiments, immediately upon addition of CrVI, a band appeared at 855 cm⁻¹ and remained for a minimum of 10 min. Synthetic CrIV/CrVI mixed oxide (Fig. 2) has a broad band at 858 cm⁻¹. As discussed above, this band is attributed to the stretches of CrO2-O bridging bonds. Assuming that the band seen at 855 cm⁻¹ is also due to the CrV-O stretch, it is reasonable to assert that CrIV species can form on copper and that they can be detected with Raman spectroscopy. Although no such band appeared in spectra of the copper substrate in the experiments described in the preceding paragraphs, a small band at 800 cm⁻¹ can be detected in Fig. 3 in the spectra acquired at t = 9.6 h and t = 14.5 h. The small band is not currently identified, but several CrIV species scatter in that general region and it is possible that the small 800 cm⁻¹ band arose from some type of CrVI species.

Two other bands in Fig. 3 merit discussion. The band appearing late in the series at 273 cm⁻¹ is possibly due to Cl⁻ contamination from the reference electrode. Several metal-chloride stretches appear in this region including Cr-Cl at 268 and Cu-Cl at 290 cm⁻¹. When the cell was manually flushed with 100 mM K2SO4 while maintaining potential control, the band at 273 cm⁻¹ disappeared. The band at 981 cm⁻¹ is attributed to the presence of sulfate within the film. Spectra of the sulfate electrolyte show its totally symmetric stretch as a strong, sharp band at 981 cm⁻¹ while the spectrum of chromium alum exhibits this stretch at 987 cm⁻¹. Pajev et al. assigned a band centered at 974.8 cm⁻¹ to sulfate ions doped in K2CrO4. It seems probable that the broad nature of the sulfate band shown in Fig. 3 indicates the presence of several sulfate spe-
interest of brevity only experiment 1 is discussed. The integrated area between 6.3 and 16.9 h (from the time of injection) is slightly more than twice the integrated area during the first 5.7 min after the injection. Again, the Clark et al. estimation of 1.6 × 10⁻³ C/cm² or 5.4 nmol/cm² for the formation of a CrIII monolayer from CrVI solution was used to estimate the coverage of the CrIII film.7 Assuming that the Cl⁻ ions are not necessary for the growth of the CrIII oxyhydroxide film. A SERS experiment was performed in all ways identical to the experiment which produced the spectra in Fig. 3 with two exceptions: the electrolyte was 100 mM NaCl and the electrode was held at −540 mV, the approximate OCP of AA-2024 T3 in 100 mM NaCl. Spectra from this experiment showed the same slow growth of a virtually identical CrIII band, albeit slightly shifted to a center of 566 cm⁻¹ compared to a center of 575 cm⁻¹ for the K₂SO₄ experiments.

Figure 4 shows the results of chronoamperometry experiments with a copper electrode subjected to identical conditions as those used in the SERS experiment which produced the spectra of Fig. 3. This experiment was performed three times over a period of one month to test reproducibility. Additionally, each experiment was started at a different time of the day to exclude the possibility of environmental influence such as light and temperature fluctuations. The electrode was roughened and the cell was established as noted above with the copper electrode held at −200 mV. After 37.6 min, 800 mM Cr³⁺ was injected to the cell concentration to −5.5 mM Cr³⁺. As in similar experiments performed by Clark et al., after the injection a large reduction spike appeared, indicating the reduction of Cr³⁺ to Cr³⁺ on the electrode surface.6 Combining the chronoamperometry experiments with the SERS experiment supports the theory that the formation of a Cr³⁺ film inhibits the reduction of oxygen through adsorption to oxygen reduction sites. The reduction current before injection of Cr³⁺ to the cell has been attributed to oxygen reduction.6 7 min after the Cr⁶⁺ injection, at the same time that the SERS spectrum started to show a loss of Cr⁶⁺ character, the reduction current had decreased by 74% in experiment 1, 60% in experiment 2, and 85% in experiment 3 compared to the current before the Cr⁶⁺ injection. After 85 min, when the SERS spectrum showed no discrete Cu₂O bands and the 575 cm⁻¹ band was established, the reduction current had decreased by 91, 93, and 97%, respectively. Table I outlines the reduction current for experiment 1. As can be seen in Fig. 4, outlines for experiments 2 and 3 would be very similar.

Inset 2 of Fig. 4 shows an unexpected but reproducible temporary increase in current beginning approximately 6-10 h after the injection of Cr⁶⁺. Although observed in all three experiments, in the

<table>
<thead>
<tr>
<th>Time elapsed from injection</th>
<th>Reduction current (μA)</th>
<th>Percent decrease in reduction current</th>
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<tr>
<td>−1 s</td>
<td>−2.415</td>
<td>⋯</td>
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<tr>
<td>7 m</td>
<td>−0.634</td>
<td>73.7</td>
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<tr>
<td>85 m</td>
<td>−0.217</td>
<td>91.0</td>
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<td>4.1 h</td>
<td>−0.136</td>
<td>94.4</td>
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<td>7.0 h</td>
<td>−0.121</td>
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<td>9.6 h</td>
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<tr>
<td>14.5 h</td>
<td>−0.073</td>
<td>97.0</td>
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<tr>
<td>23.7 h</td>
<td>−0.010</td>
<td>99.6</td>
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Table I. Current values from chronoamperometry data of Fig. 4, experiment 1.
The cell, an approximate monolayer of a CrIII film formed and strongly inhibited, but did not completely eliminate, oxygen reduction. As the film continued to form, the reduction of both oxygen and CrVI contributed to the overall reduction current. Both the reduction of oxygen and the reduction of CrVI increased the pH at the electrode surface. After approximately 5-10 h, a critical pH value was reached at the surface and the reduction of CrVI increased for reasons discussed below, and thereby more CrIII formed on the electrode surface. As the film thickened, however, both the further reduction of CrIII and oxygen reduction were severely inhibited and the overall reduction current dropped to almost zero. Fig. 5 illustrates this sequence of events.

Why would a rise in pH increase the rate of CrVI reduction? Stunzi et al.’s extensive studies of the hydrolytic polymerization of CrIII ions bear on this question.30-33 As noted in their studies, CrIII almost exclusively and constantly maintains octahedral coordination, with water molecules filling in any of the six positions not otherwise occupied. Although when compared to other metal ion octahedral complexes, CrIII complexes are inert, these studies investigated the relative rates of substitution leading to the formation of CrIII dimers and the further formation of various oligomers. Specifically, Stunzi et al. found that deprotonation of complexed water molecules induces a conjugate base effect which leads to significant increases in the rate of replacement and exchange of water molecules at CrIII centers, which in turn increases the rate of oligomer formation.32,33 Furthermore, King et al. discussed the rapid formation of Cr(CrO4)(H2O)2 and Cr(HCrO4)(H2O)2+ in solutions of CrII and CrVI ions.34 They propose that no breakage of the CrVI-O bond occurs, but rather the CrVI-O bond breaks and CrVI bonds with O-CrIII to make CrVI-O-CrIII. The formation of similar bonds with the polymerizing CrIII film could then ultimately lead to the reduction of bonded CrIII. It is, therefore, suggested that the increase in pH brought on by the potential controlled reduction of both oxygen and CrVI could provide a driving force for the further reduction of CrVI as a CrIII film polymerizes, explaining the temporary increase in reduction current seen in all three experiments of Fig. 4.

As previously noted, the copper substrate in the above experiments was held at −200 mV vs. Ag/AgCl, which is the approximate OCP of AA-2024 T3 in 100 mM K2SO4. To better understand the stability of the CrIII film, a series of four experiments identical to the SERS experiment, which produced the spectra of Fig. 3, was performed. In each case, the copper substrate was held at −200 mV vs. OCP, and CrVI was added to bring the cell CrIII concentration to −5.5 mM, and the CrIII film was allowed to grow for 19-24 h at −200 mV. Acquired spectra from this initial stage of all four experiments showed essentially the same results as Fig. 3. After 19-24 h, the cell was manually flushed while maintaining the copper electrode at −200 mV until a final CrVI concentration of −14 μM CrVI was reached. At this concentration, the cell is no longer acidic and has a pH of −7.1. After the cell was flushed, for each of the four experiments, respectively: (i) the potential was left at −200 mV, (ii) the potential was increased to −150 mV, (iii) the potential was increased to −100 mV, or (iv) potential control was turned off and the cell was allowed to drift to its OCP, which was previously determined to be approximately −63 mV. In each of these four experiments, the flushed cell was maintained under its respective potential for 5.7 h. Spectra were acquired both before and after this holding period. The plot in Fig. 6 was created using four replicate spectra from each of the four experiments. Two of the four spectra were acquired immediately before the cell was flushed and two of the spectra were acquired at the end of the 5.7 h. The spectra were baseline corrected by leveling between 365 and 760 cm−1, and the area of the 575 cm−1 band was determined by integrating between these same endpoints. Galactic’s Grams spectral software (version 4.02) was used to perform baseline adjustments and all integrations. Figure 6 shows the percent of the 575 cm−1 band area retained after 5.7 h at each respective holding potential, relative to the 575 cm−1 band area before the cell was flushed. The film remained stable at −200 mV, however, as the holding potential increased, the area of the 575 cm−1 band decreased, indicating less stability for the CrIII film at more positive potentials. Compared to the OCP of AA-2024 T3 under most field conditions, a potential of −200 mV is relatively high. For example, the measured OCP of AA-2024 T3 in 100 mM NaCl is −540 mV. Therefore, although the CrIII film is only a few

**Figure 5.** Sequence of events during formation of CrIII film.
monolayers thick, under near neutral pH conditions and potentials of about 200 mV vs. Ag/AgCl, it is chemically stable.

A chromium-containing layer of a few monolayers differs greatly in thickness from the several micrometer thick CCC, even though they both originate with CrVI in solution. Alodine 1200 solution has a much higher CrVI concentration (~40 mM) than that studied here, and the Fe(CN)₆³⁻ “accelerator” generates a high concentration of CrIII during CCC formation. The CrIII polymerized slowly due to the low pH, so that a sol-gel was formed, containing both CrIII and CrVII. It is likely that many CrVII-O-CrIII bonds were formed in such a sol-gel, and they may have been reduced to CrIII-O-CrIII or been incorporated into the CCC as CrIII/CrVII mixed oxide. The fact that CrVII is more labile to substitution than CrIII is consistent with an important role of the CrVII-O-CrIII linkage in CCC formation. The lability of CrVI vs. the inertness of CrIII is illustrated by the well-established fast equilibrium: 2HCrO₄⁻ ↔ Cr₂O₇²⁻ + H₂O, and the very low exchange rate constant of H₂O at a CrIII center of ~10⁻⁷ s⁻¹.³⁵ As the sol-gel continued to cross-link, Fe(CN)₆³⁻ and F⁻ mass transport were presumably decelerated and the CCC thickness became self-limiting. The main factors promoting thick CCC formation are low pH, presence of Fe(CN)₆³⁻, high Cr III concentration, and the constant exposure of bare aluminum by F⁻ ion etching. The dilute CrIII solution studied in the current work had none of these factors present, so electron transfer to either oxygen or CrVII was inhibited by only a few monolayers. It should be emphasized that both CCC formation and redox inhibition by dilute CrVII depended on the critical CrVII-O-CrIII intermediate.

Conclusions

The copper-rich intermetallics that add strength to aluminum alloys make them particularly susceptible to localized corrosion in part by providing cathodic sites for oxygen reduction. The current work provides spectroscopic evidence that a CrIII oxyhydroxide film forms on copper exposed to chromate and that this film severely inhibits oxygen reduction on copper. Although oxygen reduction inhibition is a clear effect of the CrIII film, its general inhibition of electron transfer may also interfere with oxidation reactions associated with anodic dissolution.³⁶-³⁸ At a potential of ~200 mV vs. Ag/AgCl, a near monolayer of substitution inert CrIII is established on a copper surface within minutes after its exposure to CrVI solution, and this initial layer decreases oxygen reduction on the copper sites by >70%. Over a period of several hours the further reduction of CrIII continues to contribute to the CrIII film thickness on the copper surface, with further inhibition of oxygen reduction. The binding of labile CrVII to the CrIII centers of the film serves to concentrate CrVI at the alloy surface, and it may provide a conduit for transferring electrons from the alloy to CrVI. As the CrIII film thickens, it effectively shuts down both oxygen reduction and further CrVII reduction. Under neutral pH conditions and OCP, encountered in field applications, this substitution inert CrIII film is stable. Furthermore, a CCC or CrVI containing primer provides a ready source of mobile CrVI which can adsorb and reduce at defects to effect “self-healing.” Perhaps the most important and distinctive feature of CrVI is its transition upon reduction from a mobile, substitution labile form to insoluble, substitution inert CrIII. The spectroscopic results clearly support a mechanism based on rapid, irreversible CrVI reduction at cathodic sites, slow subsequent adsorption and reduction of CrVI to CrIII, and eventual formation of a self-limiting layer with a thickness of several CrIII monolayers. The substitution rates of CrIII and CrVI are critical to the process as is the existence of the CrIV-O-CrIII linkage during Cr deposition. The product of dilute CrVI interactions with AA-2024 T3 inhibits electron transfer in general, and particularly oxygen reduction on what had been cathodic sites.

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