XANES STUDIES OF CHROMATE REPLACEMENTS IN OXIDE FILMS ON ALUMINUM

A. J. Davenport, A. J. Aldykiewicz Jr., and H. S. Isaacs
Applied Physics Division, Brookhaven National Laboratory
Upton, NY 11973

M. W. Kendig
Rockwell International Science Center
Thousand Oaks, CA 91360

A. M. Mundy
Half Hollow Hills High School
Dix Hills, NY 11746

The chemistry of conversion coatings on aluminum containing chromate and non-toxic chromate replacements has been investigated using XANES. Chromate conversion coatings contain 20% 6-valent chromium which is gradually lost on immersion in a corrosive environment. The most promising alternative coatings are those based on phosphotungstate. The chemistry of these and coatings containing Mo, V, and Mn are discussed.

INTRODUCTION

Chromate is widely used both as an inhibitor and in corrosion-resistant coatings for aluminum and its alloys. Although it is highly effective in combatting corrosion, there is considerable interest in its replacement due to its toxicity. In this paper, X-ray Absorption Near Edge Structure (XANES) is used to investigate the chemistry of chromium in freshly-formed conversion coatings on aluminum alloys and after exposure of coated alloys to a chloride solution. The chemical changes are compared with those found for a number of less toxic coating systems based on tungsten, molybdenum, vanadium, and manganese.

XANES is an effective technique for the study of inhibiting species in oxide films on metals. The valence state of species present at very low concentrations (equivalent to a few monolayers) can be determined in air, in an electrochemical cell or under a polymer coating. It has already been used to study the role of chromate (1,2) and cerium ions (2-4) as corrosion inhibitors for aluminum. In addition, XANES has been used to study the valence state of chromium in films on aluminum formed by anodizing in chromate solution (5,6) as well as in anodized films on aluminum grown in chromium-free solutions then subsequently sealed in a dichromate

solution (7). Open circuit exposure of aluminum with an air-formed film to chromate solutions yields 3-valent chromium in the film. As the oxide film on aluminum thickens by anodizing, the proportion of 6-valent chromium in the film increases (1). Anodizing aluminum in chromate solutions yields a mixture of 3- and 6-valent chromium, the latter being found in the outer part of the film (2,5,6). Sealing an anodized aluminum film in dichromate yields entirely 6-valent chromium (7). It has been proposed that the reduction of chromium from the 6-valent state to the 3-valent state takes place at flaws in the film, which are more numerous for thinner films so the proportion of 3-valent chromium is expected to be higher for thinner films (1).

EXPERIMENTAL

The mechanism of formation of chromate conversion coatings was investigated by immersing 3"x3" coupons of Al 2024-T3 to an Alodine 1200S chromate bath for times varying between 1 and 30 minutes. For studying the degradation of conversion coatings, Alodine 1200S-treated Al 3003 panels (Q-Panel) were immersed in aerated 0.5M NaCl for periods up to 1 month. XANES spectra were collected for all the samples.

Non-chromate conversion coatings were formed on Al 1100 panels 75mmx75mmx2mm. These were cleaned by immersion in 8% NaOH for 2 minutes followed by immersion in 50% HNO_3 for 30 seconds, rinsed in distilled water (Millipore-Q) and dried in a stream of nitrogen. The coatings were formed in a bath containing 0.1M metal ions, 4g/l HF for 10 minutes at 60°C, the pH having been adjusted to the desired value (2, 4, or 6) with H_3PO_4 or NaOH. The metal ions used were vanadate, tungstate, phosphotungstate, tungstosilicic acid, molybdate, phosphomolybdate and molybdosilicic acid. These were used either alone or in combination such that the total concentration of metal ions in the solution was 0.1M. One side of each sample was exposed for 48 hours in aerated 0.5M NaCl. XANES meaurements were made of both exposed and unexposed sides, which were compared visually to assess the extent of corrosion.

The non-chromate conversion coatings prepared in the laboratory were compared with a commercial Mn-containing coating from Sanchem. In addition, a sample was prepared by immersing Al 1100 in a dilute solution of $KMnO_4$.

XANES measurements were made at Beamline X11A at the National Synchrotron Light Source at Brookhaven National Laboratory. The oxide films were measured in fluorescence geometry with an incident angle of ~3° to give a large surface area of illumination by the beam and reduce scattering from the underlying metal. The absorption coefficient was taken as (I_f/I_o) where I_f is the fluorescent intensity and I_o is the incident intensity (both were measured using ion chambers).

Standard compounds were crushed to form fine powders which were spread thinly and sealed between adhesive Kapton tape. These, together with thin metal foils, were measured in conventional transmission geometry (the absorption coefficient is $\log(I_o/I_t)$ where I_t is the transmitted intensity).

RESULTS AND DISCUSSION

Fig. 1 shows XANES for a series of standard compounds of chromium illustrating the change in edge position and features with valence state. They are normalized to the edge height at 100-200eV above the edge. Metallic chromium shows the lowest energy edge. Its edge position, $E_o=5989eV$, is defined as the position of the first maximum in the derivative of the metal spectrum. The positions for features on the edge are quoted relative to E_o. Cr_2O_3, a 3-valent chromium compound, has an edge position at an energy higher than E_o with a double-peaked maximum in absorption at ~20eV. K_2CrO_4, a 6-valent chromium compound, has the highest edge position. It also has a distinctive sharp peak below the edge at +4eV. The height of this peak is close to the edge height. The peak is due to the non-centrosymmetric tetrahedral co-ordination found for 6-valent chromium compounds (8), but is absent for lower-valent species which are typically octahedrally co-ordinated.

The pre-edge peak found for 6-valent chromium provides a valuable fingerprint for 6-valent chromium even in the presence of different valent species. The ratio of the pre-edge height to the edge height can be used to estimate the proportion of 6-valent chromium in a mixture of the 6- and 3-valent species. Fig. 2 shows a calibration curve. The solid symbols are data taken from mixed powders of K_2CrO_4 and Cr_2O_3 with known compositions. The open symbols were calculated by taking a linear combination of the spectra of pure K_2CrO_4 and Cr_2O_3 in known proportions. There is an approximately linear relationship which holds particularly well at low Cr(VI) contents.

Fig. 3 shows a number of edges taken from unexposed 3003 panels with a chromate conversion coating illustrating the good reproducibility from sample-to-sample. From the ratio of the pre-edge peak height to the edge height, it can be determined that the ratio of 6-valent to total chromium in these samples is ~23%.

Fig. 4 shows data from a series of Al 2024-T3 panels which have been exposed to the conversion coating processing bath for different lengths of time. The edge height (which is proportional to the total amount of chromium present) and the percentage of 6-valent chromium (determined from the ratio of the pre-edge peak height and the edge height and the calibration curve in Fig. 2) are shown in Fig. 4(a) and Fig. 4(b) respectively. Both values increase with time for 5 minutes after which they reach a plateau.

Data were obtained for a set of commercially-prepared conversion coatings on Al 3003 which were exposed to 0.5M NaCl for different lengths of time. Fig. 5(a) shows a steady decrease in edge height with exposure time indicating a loss of total chromium present. Fig. 5(b) shows that the proportion of 6-valent chromium decreases with time. This suggests an explanation as to why chromate is such an effective inhibitor. In addition to producing a protective film which is predominantly insoluble 3-valent chromium, a proportion of the chromium (>20%) remains in the film in the 6-valent state which can be used to plug flaws in the film as they develop and is thus slowly consumed.

Of the non-chromate conversion coatings, those prepared at pH 4 appeared by visual inspection to be most resistant to corrosion, closely followed by those prepared at pH 6. At pH 2 little coating seemed to be formed and the extent of corrosion was usually severe. There were no differences in the shape of the XANES for any of the films before and after exposure. This contrasts with chromium where the proportion of 6-valent chromium diminishes on exposure. However, the edge height, which is proportional to the elemental concentration, was often considerably less after exposure due to loss of the film, so the edges shown here will all come from unexposed parts of the sample.

Visual inspection indicated that coatings containing tungstophosphate, either alone or in combination with vanadate showed the greatest corrosion resistance. Fig. 6 shows a typical W L_3 absorption edge for an unexposed tungstophosphate-containing film. Superimposed on the edge are a number of 6-valent standard compounds of tungsten measured in transmission in the form of powders. They have been normalized to give the same edge step well above the edge. The only significant difference is between the height of the main peak or white line. This is an artifact of the transmission measurements due to the effect of sample thickness. However, the close coincidence of the position of the main peak indicates that the tungstophosphate film contains tungsten in the +6 valence state.

All the films formed containing vanadium showed a very similar edge shape. This is illustrated in Fig. 7 which shows the edge from a sample formed in a mixture of vanadate and tungstophosphate. Superimposed on the edge are edges from 4- and 5-valent standard compounds of vanadium. The edge position and pre-edge peak height both coincide with the 4-valent compounds VO_2 and $VOSO_4$ rather than the 5-valent vanadate which was the starting compound, indicating that the vanadate is reduced during film formation. However, this reduction may not be as beneficial as that which takes place on reduction of chromate as 4-valent vanadium is more soluble than 3-valent chromium. A more soluble species is likely to dissolve from the film and thus lose its effect. The 5-valent vanadium compound may serve as a "chemical anodization" reagent.

All the films made from molybdenum-containing species gave similar K edge structure, an example of which is shown in Fig. 8 together with standard compounds. From the latter, it is clear that molybdate ions give a different edge shape than the polymeric ions molybdophosphoric acid and molybdosilicic acid. For molybdate, the pre-edge peak is much more distinct whereas for the polymeric species, the pre-edge feature is a much smaller shoulder. The conversion coatings all give Mo K edges which have the same shape as the polymeric species, even those formed from molybdate solution. This suggests that incorporation of molybdate into the coating involves no change in valence state but rather formation of a 6-valent polyanion. Films formed in solutions containing vanadium and molybdenum show very small Mo K edges implying that vanadate prevents incorporation of molybdenum in the film.

Immersion of Al 1100 in $KMnO_4$ solution results in reduction of the manganese to the +4 valence state. This is shown in Fig. 9 where the Mn K edge from the film is superimposed with the edge of MnO_2. Fig. 10 shows the Mn K edge from a commercially-prepared conversion coating (Sanchem) which shows good corrosion resistance. The position of the main peak on the edge coincides with that of MnO_2. However, the start of the edge coincides with that of manganese metal, significantly lower in energy than that found for any other valence state of manganese. This suggests that the manganese may be present both in the metallic state and a 4-valent form similar to MnO_2.

CONCLUSIONS

1. The ratio of hexavalent Cr to total Cr in conversion coatings exceeds 0.2 suggesting that Cr(VI) reamins a major constituent of chromate conversion coatings on Al and Al alloys.

2. With environmental exposure to aerated 0.5M NaCl, both the concentration of chromium and the relative concentration of Cr(VI) in the film diminish with time.

3. The thickness and Cr(VI) concentration of a conversion coating on Al 2024-T3 reaches a limit after about 5 minutes of processing.

4. Tungstophosphate, both alone and in combination with vanadate looks to be the most promising substitute for chromate in the formation of a conversion coating. Tungsten remains in the 6-valent state on incorporation in the film.

5. Vanadate undergoes reduction to a 4-valent species on incorporation into conversion coatings.

6. Molybdate undergoes no valency change but probably forms a polymeric

species on incorporation in conversion coatings. The presence of vanadate in the bath prevents incorporation of molybdenum in conversion coatings.

7   Immersion of Al-1100 in $KMnO_4$ leads to formation of a film containing MnO_2. A commercially-produced Mn-containing coating (Sanchem) contains both MnO_2 and zero-valent manganese.

ACKNOWLEDGEMENTS

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DISCLAIMER

Fig. 1 Cr K edge relative to $E_0 = 5989$eV for chromium foil and powders of Cr_2O_3 and K_2CrO_4 measured in transmission. The edges have been normalized to the step height at +100-200eV.
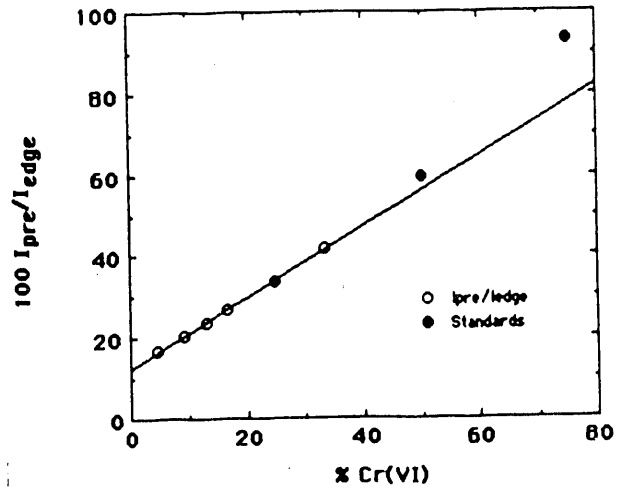
Fig. 2 Ratio of pre-edge peak height to edge height for calculated (open symbols) and measured (solid symbols) mixtures of Cr_2O_3 and K_2CrO_4.
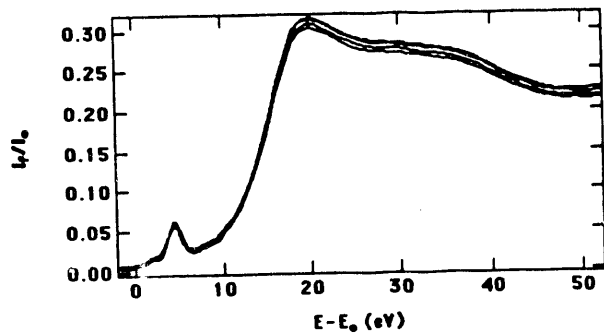
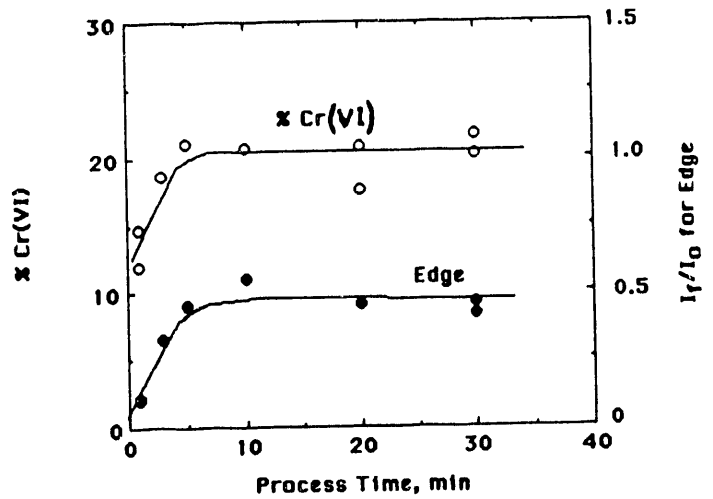Fig. 3 Cr K edges for four Al 3003 panels with commercially-prepared chromate conversion coatings illustrating reproducibility.

Fig. 4 (a) edge height and (b) %Cr(VI) for Al 2024-T3 panels immersed in a chromating bath for the times indicated.
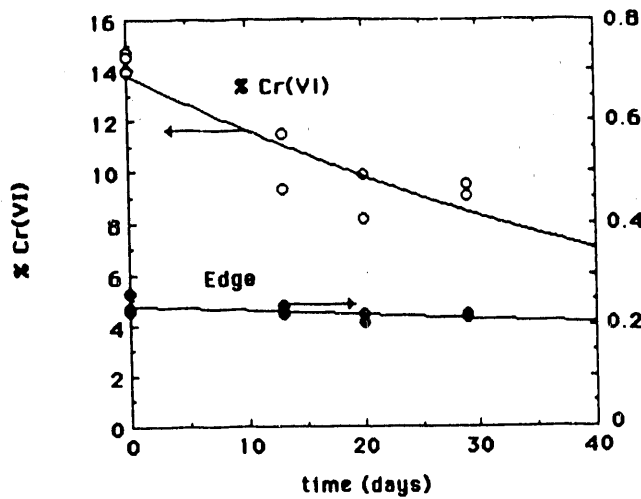
Fig. 5 (a) edge height and (b) %Cr(VI) for Al 3003 panels with a commercially-prepared chromate conversion coating immersed in aerated 0.5M NaCl for the times indicated.
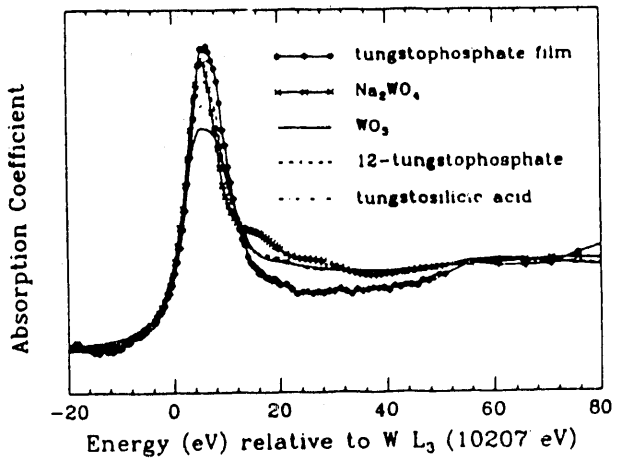
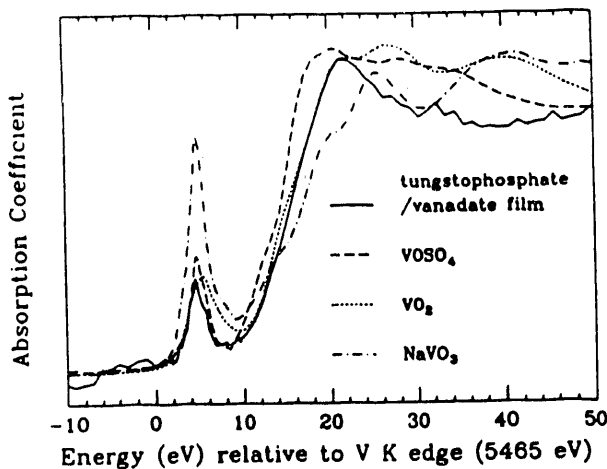Fig. 6 W L$_3$ edge (E$_0$=10207eV) for a film formed in a tungstophosphate bath compared with standard compounds.

Fig. 7 V K edge (E$_0$=5465eV) for a film formed in a tungstophosphate/vanadate bath compared with standard compounds.

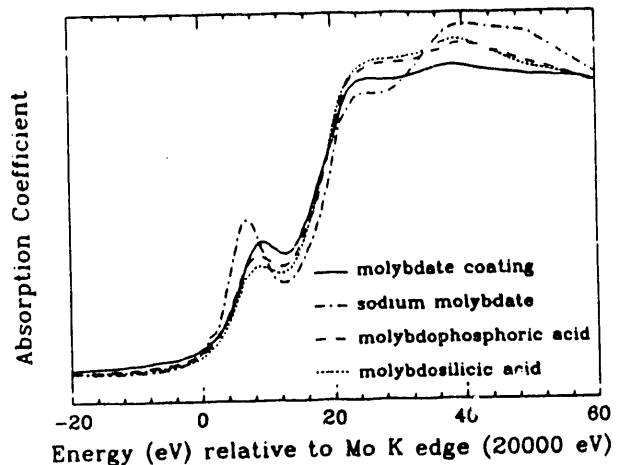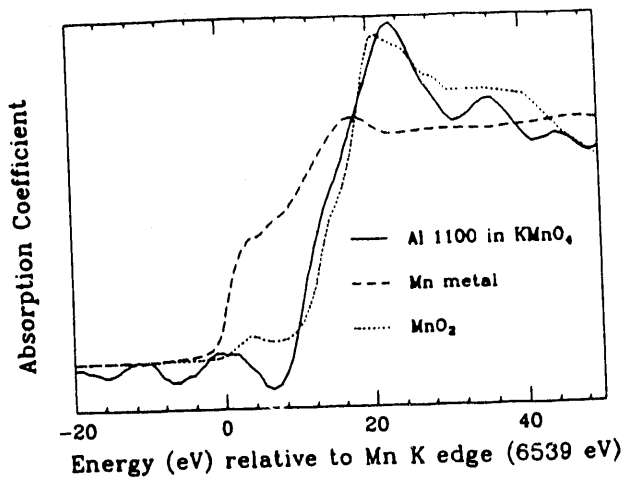Fig. 8 Mo K edge (E$_0$=2000eV) for a film formed in a molybdate bath compared with standard compounds.

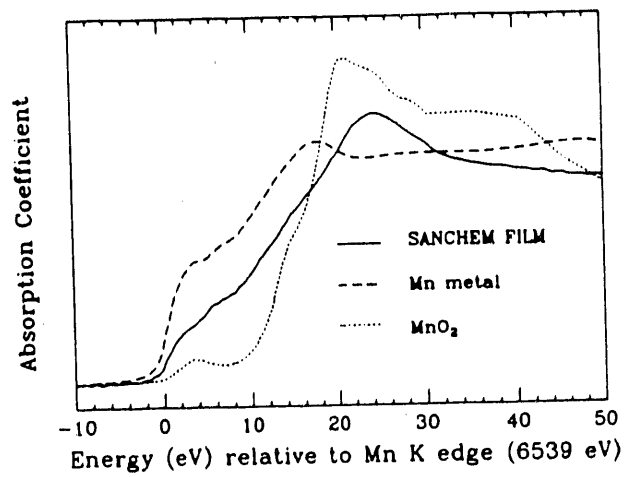Fig. 9 Mn K edge (E_o=6539eV) for a film formed by immersion in dilute $KMnO_4$ compared with Mn metal and MnO_2.

Fig. 10 Mn K edge (E_o=6539eV) for a commercially-prepared conversion coating (Sanchem) compared with Mn metal and MnO_2.

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