X-ray photoelectron spectroscopy studies of reactions on chromium metal and chromium oxide surfaces

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**Abstract**

This paper reports several interrelated XPS investigations of the Cr–O system that provide additional interpretation of the Cr 2p\(_{3/2}\) spectra, along with more detail on the reaction mechanisms between O\(_2\) gas and H\(_2\)O vapour with metallic Cr. The Cr 2p\(_{3/2}\) spectra of polycrystalline Cr\(_2\)O\(_3\) contain multiplet structures that bear a strong resemblance to those calculated by Gupta and Sen for the free Cr\(^{3+}\) ion. The O/Cr ratio derived from the corrected Cr\(^{3+}\) and substitutional O\(^{-}\) intensities for all polycrystalline Cr\(_2\)O\(_3\) samples was 1.5. Annealing of freshly cleaved polycrystalline Cr\(_2\)O\(_3\) surfaces above 550 °C resulted in a sharpening of the multiplet structures that may be caused by the increased prevalence of the (0001) Cr\(_2\)O\(_3\) orientation on the surface. The slight difference in binding energies between the low energy (0001) plane and the other major crystallographic orientations could contribute to the spectral broadening that is observed for the Cr 2p\(_{3/2}\) spectral line shapes. The Cr 2p\(_{3/2}\) spectrum for Cr(OH)\(_3\) was isolated from that produced by Cr\(_2\)O\(_3\) and the multiplet structure was qualitatively re-assembled for that of the hydroxide. The Cr 2p\(_{3/2}\) and O 1s spectra of reaction products on polycrystalline metal surfaces were analysed using the above information. The oxidic portion of the Cr 2p\(_{3/2}\) spectra could be cleanly separated from the metallic substrate using spectral subtraction. Reactions of either O\(_2\) gas or H\(_2\)O vapour both produced a thin Cr\(_2\)O\(_3\) film that was deficient in Cr\(^{3+}\) and, depending on the reactant, showed varying concentrations of hypo-stoichiometric Cr moieties. The surface corrected O/Cr ratios calculated for all the oxidised surfaces were 1.7. There was little evidence to support the formation of Cr(OH)\(_3\) on these surfaces. For comparison, an aqueous reaction of a Ni–Cr (20%) alloy was studied where both Cr(OH)\(_3\) and Cr\(_2\)O\(_3\) components could be analysed. For this example no sub-stoichiometric Cr oxide species were produced.

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**1. Introduction**

An understanding of the reactions that occur on Cr surfaces is important as the element is added to many materials to increase their corrosion resistance. At temperatures below 400 °C thin Cr\(_2\)O\(_3\) film growth on metallic Cr has been shown to follow a Cabrera–Mott model [1–6], where oxidation is driven by an electric field created by electrons tunnelling through the oxide film from the Cr metal substrate. Cations and/or anions are mobile in this electric field and move through defect sites and grain boundaries, resulting in the formation of thin oxide films [1–5]. It has been shown that Cr\(_2\)O\(_3\) is primarily a p-type oxide where cations are most mobile, however some anion migration has also been identified [1–6].

This paper presents an XPS study of Cr metal surfaces following reactions with O\(_2\) gas, H\(_2\)O vapour, and in an aqueous solution. This work was done to provide a more complete base for the subsequent study of surfaces of a Ni–Cr (20%) alloy subjected to aqueous corrosion at controlled electrochemical potentials and temperatures. XPS is useful for such studies as it provides both compositional and chemical state information over an information depth of ∼5 nm – a thickness encompassing both the metal substrate and the surface oxides. The XPS spectra of Cr oxides are rich in additional structure from multiplet splitting; previous papers have provided significant details on these spectral structures [7–11], but additional information regarding both Cr\(_2\)O\(_3\) and Cr(OH)\(_3\) spectral features and elemental intensity ratios have been obtained in this work. Using this information, surfaces of polycrystalline Cr metal following gas phase reactions with O\(_2\) or H\(_2\)O at 300 °C could be shown to contain a sub-stoichiometric Cr\(_2\)O\(_3\) (Cr\(_{2+x}\)O\(_{3-y}\)) component. By contrast, during aqueous oxidation of...
a Ni–Cr (20%) alloy, only Cr₂O₃ and Cr(OH)₃ contributions were detected.

2. Experimental

All XPS analysis was carried out using a Kratos Axis Ultra spectrometer employing a monochromatic Al Kα (15 mA, 14 kV) X-ray source. The work function and the dispersion of the instrument were calibrated to give metallic Au 4f7/2 and Cu 2p3/2 signals of 83.95 eV and 932.63 eV respectively. All XPS analysis employed the hybrid-focusing lens, a scan time of 180 s, and an analysis area of 700 μm × 300 μm. Differential surface charging on insulating samples was minimised using the Kratos charge neutraliser system with a filament current between 1.7–1.8 A and a charge balance of 2.8 V. Survey spectra were collected at a pass energy of 160 eV with a 0.7 eV energy step over a binding energy (BE) range of 1100–0 eV. Analyses of the Cr 2p, O 1s and C 1s envelopes were carried out at a pass energy of 20 eV, an energy step size of 0.05 eV, over energy ranges of 595–565 eV (30–70 sweeps), 540–520 eV (5–15 sweeps), and 295–275 eV (10–20 sweeps) respectively. Pressures near 5 × 10⁻⁹ Torr were observed in the analytical chamber during surface analysis.

A polycrystalline Cr₂O₃ powder was obtained from Sigma Aldrich having 99.9% purity. Polycrystalline Cr₂O₃ aggregates (∼2–3 mm in size) and polycrystalline Cr metal pieces (1–25 mm in size) were obtained from Alfa Aesar having purity levels of 99.6% and 99.9% respectively. A Ni–Cr (20%) rod was obtained from ACI Alloys Incorporated. Samples of a Cr₂O₃ powder were pressed into a double-sided, non-conducting polyethylene polyimide prior to XPS analysis to minimise the chance of differential surface charging. The Cr₂O₃ aggregates were fractured under vacuum in a chamber having a base pressure of 1 Torr, 6.0 × 10⁻⁹ L/s 286.2 ± 0.1 eV and 288.6 ± 0.2 eV [17]. A small peak was found at 289.6 ± 0.2 eV on all of the oxidised metallic Cr samples, while a very distinct separation between the 2p3/2 and 2p1/2 peaks was observed on all survey spectra. The RSF values for the O 1s and C 1s spectra were 0.780 and 0.278 respectively. Fitting of the high-resolution spectra was completed using components having mixed Gaussian–Lorentzian character. The Cr 2p3/2 envelopes were best fit using Gaussian (40%)–Lorentzian (60%) line shapes, which are denoted as GL(60) in CasaXPS. The O 1s and C 1s regions were best fit using Gaussian (40%)–Lorentzian (60%) line shapes, which are denoted as GL(60) in CasaXPS. The O 1s and C 1s regions were best fit with components having Gaussian–Lorentzian profiles respectively. To compare the different Cr, O, and C species present the total atomic concentrations (see Table 1) were corrected using the peak area ratios obtained from the fitting of the respective high-resolution spectra (see Tables 2–4). All specimens studied as a part of this work were found to contain significant amounts of adventitious C (see Table 1). A representative C 1s spectrum collected from the Cr₂O₃–2 powder sample is shown in Fig. 1. All C 1s spectra were dominated by a strong hydrocarbon (C–C, C–H) signal, which was used for spectral calibration of insulating samples and corrected to a BE of 284.8 ± 0.1 eV. Additional spectral intensity assigned to alcohol/ether ((–COH, –CO–, –OH, –CO–O–) carbonyl (–CO–), and ester (–C(=O)–) functionalities were also observed at respective BEs of 286.2 ± 0.1 eV, 287.7 ± 0.1 eV, and 288.6 ± 0.2 eV [17]. A small peak was found at 289.6 ± 0.2 eV on all of the oxidised metallic Cr samples and attributed to a carbonate (–CO₂⁻) species. A previous publication by this group had assigned the peak at 286.2 ± 0.1 eV solely to a –COH group [15]. For the above peak assignments to be valid a minimum area ratio of 1:1 was required between the components centered at 286.2 ± 0.1 eV and 288.6 ± 0.2 eV. In cases where the intensity of the lower BE peak was found to be greater
<table>
<thead>
<tr>
<th>Sample</th>
<th>Total C 1s (at.%</th>
<th>Contributions from C to the C 1s spectra</th>
<th>Total O 1s (at.%</th>
<th>Calculated contributions from O to the O 1s spectra</th>
</tr>
</thead>
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<td></td>
<td></td>
<td>–COH/–COC(0=C(=O–C*)) C(O–C*)– CO–</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 1s (%) at.% x</td>
<td>at.%</td>
<td>C 1s (%) at.%</td>
</tr>
<tr>
<td>Cr₂O₃-1</td>
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<td>19.2</td>
<td>0.9</td>
<td>4.6</td>
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<td>Cr₂O₃-4</td>
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<td>0.2</td>
<td>0.3</td>
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<td>Cr(OH)₃·xH₂O</td>
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<td>7.9</td>
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<td>6.0</td>
<td>1.3</td>
<td>4.1</td>
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<td>NiCr metal</td>
<td>33.2</td>
<td>6.1</td>
<td>0.3</td>
<td>1.7</td>
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</table>

* Carbon atom giving rise to the C 1s signal.

a Normalised surface C concentration for the O=C(O–C*) group.
b Combined normalised surface C concentration for the assumed 1:1 mixture of –COH/–COC– species.
c The normalised surface O concentration could be calculated using either the O=C(O–C*) or O=C– values from the C 1s analyses.
d The normalised surface O concentration for the assumed 1:1 mixture of –COH/–COC– species was estimated using an O/C ratio of 2:3.

### Table 3

Cr 2p₃/₂ peak fits for the polycrystalline Cr₂O₃, Cr(OH)₃, and Cr metal samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM (eV)</th>
<th>Peak 1 (eV)</th>
<th>Area (%)</th>
<th>Peak 2 (eV)</th>
<th>Area (%)</th>
<th>Peak 3 (eV)</th>
<th>Area (%)</th>
<th>Peak 4 (eV)</th>
<th>Area (%)</th>
<th>Peak 5 (eV)</th>
<th>Area (%)</th>
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<tr>
<td>Cr₂O₃-1</td>
<td>1.05</td>
<td>575.4</td>
<td>34.2</td>
<td>576.4</td>
<td>29.4</td>
<td>577.1</td>
<td>22.1</td>
<td>578.0</td>
<td>9.1</td>
<td>578.8</td>
<td>5.2</td>
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<tr>
<td>Cr₂O₃-2</td>
<td>1.03</td>
<td>575.7</td>
<td>34.7</td>
<td>576.7</td>
<td>30.2</td>
<td>577.3</td>
<td>21.2</td>
<td>578.2</td>
<td>8.7</td>
<td>579.0</td>
<td>5.2</td>
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<tr>
<td>Cr₂O₃-3</td>
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<td>576.6</td>
<td>34.1</td>
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<td>30.3</td>
<td>577.3</td>
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<td>8.5</td>
<td>579.0</td>
<td>5.1</td>
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<td>Cr₂O₃-4</td>
<td>0.99</td>
<td>575.8</td>
<td>34.9</td>
<td>576.8</td>
<td>30.2</td>
<td>577.5</td>
<td>19.7</td>
<td>578.4</td>
<td>8.6</td>
<td>579.2</td>
<td>4.7</td>
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<tr>
<td>Cr(OH)₃·xH₂O oxide component</td>
<td>1.03</td>
<td>575.7</td>
<td>4.7</td>
<td>576.7</td>
<td>4.1</td>
<td>577.4</td>
<td>2.9</td>
<td>578.2</td>
<td>1.2</td>
<td>579.0</td>
<td>0.8</td>
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<tr>
<td>hydroxide component</td>
<td>1.32</td>
<td>576.3</td>
<td>28.1</td>
<td>577.1</td>
<td>23.3</td>
<td>577.8</td>
<td>21.9</td>
<td>578.5</td>
<td>9.3</td>
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<td>3.8</td>
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<tr>
<td>Cr metal</td>
<td>1.32</td>
<td>574.1</td>
<td>75.2</td>
<td>574.8</td>
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<td>576.8</td>
<td>4.5</td>
<td></td>
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</table>

a Additional peaks at 574.0±0.1 eV were also required to completely fit the Cr 2p₃/₂ spectra for the fractured and heated aggregates.
b The Cr₂O₃ contribution was estimated using the fit obtained for the Cr₂O₃-2 powder sample.
c The Cr metal Cr 2p₃/₂ spectrum was fit with 3 peaks which do not represent Cr species in different chemical environments. The envelope was fit with an asymmetric component having the line shape LA(1.3,2.3,10) and a FWHM of 0.77 eV, while peaks 2 and 3 had a line shape of GL(30) and FWHM values of 2.16 eV.
Table 4
O 1s peak fits for the Cr₂O₃, Cr(OH)₃, oxidised Cr, and oxidised NiCr metal samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak 1 (eV)</th>
<th>Area (%)</th>
<th>FWHM (eV)</th>
<th>Peak 2 (eV)</th>
<th>Area (%)</th>
<th>FWHM (eV)</th>
<th>Peak 3 (eV)</th>
<th>Area (%)</th>
<th>FWHM (eV)</th>
<th>Organics (%)</th>
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<tr>
<td>Cr₂O₃ -1</td>
<td>530.0</td>
<td>70.7</td>
<td>1.07</td>
<td>531.2</td>
<td>24.5</td>
<td>1.92</td>
<td>532.9</td>
<td>4.8</td>
<td>1.39</td>
<td>10.7</td>
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<td>Cr₂O₃ -2</td>
<td>530.3</td>
<td>69.7</td>
<td>1.04</td>
<td>531.6</td>
<td>27.6</td>
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<td>533.2</td>
<td>2.7</td>
<td>1.40</td>
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<tr>
<td>Cr₂O₃ -3</td>
<td>530.2</td>
<td>81.7</td>
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<tr>
<td>Cr(OH)₃·xH₂O</td>
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<td>4.5</td>
<td>1.02</td>
<td>531.6</td>
<td>87.5</td>
<td>1.81</td>
<td>533.5</td>
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<td>Cr(OH)₃·xH₂O</td>
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<td>Cr metal–1</td>
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<td>531.5</td>
<td>38.8</td>
<td>1.81</td>
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<td>NiCr metal</td>
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<td>1.35</td>
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<td>97.0</td>
<td>1.65</td>
<td>533.6</td>
<td>1.4</td>
<td>1.45</td>
<td>4.4</td>
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</table>

* Peak area calculated by subtracting the total organic contribution from the OH– component.

than the peak at 288.6 ± 0.2 eV the additional spectral intensity was assumed to be split equally between C atoms bound as –COH and –COC–. The organic contribution to the O 1s spectra was estimated by first calculating the surface normalised C intensities. From these intensities the corresponding normalised O concentrations were obtained using the expected O/C ratios for the individual functional groups (i.e. 1:1 for –C=O). The normalised O concentrations were then converted to the respective O 1s peak areas. This procedure is summarised in Table 2.

The CasaXPS program was also used for spectral subtractions. To simplify the analysis of the oxidised metal surfaces, the metal contribution was removed. A similar technique was previously employed by this group to study the oxidation of Ni metal [14,15,18].

3. Results and discussion

3.1. Spectral refinements for Cr₂O₃

Two samples of a polycrystalline Cr₂O₃ powder were analysed with XPS and a representative high-resolution Cr 2p₃/₂ spectrum is shown in Fig. 2(a). The spectra collected from both samples were fit with 5 peaks representing the multiplet splitting of the Cr³⁺ cations following photoionization (see Table 3). The fits produced using this approach agree well with the 2p₃/₂ line shape calculated for a Cr³⁺ free ion by Gupta and Sen [7,8,11]. Two polycrystalline Cr₂O₃ aggregates were fractured and heated (550 °C) in vacuo and the freshly fractured surfaces were analysed by XPS. The Cr 2p₃/₂ fitting results were found to be very similar to those for the polycrystalline Cr₂O₃ powder (see Table 3). Heating of the aggregates resulted in a narrowing of the 5 multiplet splitting components relative to what was observed for the polycrystalline Cr₂O₃ powder samples (see Table 3). As well, a small component near 574 eV [11] was also required to fit the envelope. A fitted representative Cr 2p₃/₂ spectrum is shown in Fig. 3(a). The observed difference in peak widths is attributed to the formation of an oxide surface that is primarily oriented in the (0001) direction following heating at 550 °C. Previous LEED studies have shown that annealing of polycrystalline Cr₂O₃ surfaces near this temperature lead to a crystal reorganisation to form the low surface energy (0001) plane [19,20].

The O 1s spectra collected for all polycrystalline Cr₂O₃ samples were fit with an O²⁻ component at 530.2 ± 0.2 eV, along with additional broad peaks at BEs ranging from 531.2 to 533.2 eV (see Table 4). Example spectra are presented in Figs. 2 and 3(b). As was shown in a previous publication, some of the intensity of the high BE peaks can be attributed to the presence of organic species associated with adventitious C [15]. The contribution of these organic...
species to the O 1s spectra have been estimated, and the results are presented in Table 4. Additional contributions from adsorbed O and/or OH surface species cannot be ruled out. Small amounts of Ca, Mg, Na, and Si (see Table 1) were also detected on the aggregate samples during compositional analysis and some of the intensity in the O 1s peaks may arise from the presence of the oxides and/or hydroxides of these species. The O/Cr ratios for the polycrystalline powder samples were calculated using the normalised surface intensities of the O\(^2\) and Cr\(^{3+}\) components and were determined to be 1.5 (see Table 5). This result indicates that the presence of significant amounts of surface Cr(OH)\(_3\) is unlikely as the calculated O/Cr ratios are identical to the expected value of 1.5 for pure Cr\(_2\)O\(_3\). A similar method was used to determine the O/Ni ratios in a previous publication (see Fig. 4 in Ref. [11]). In the original analysis it was determined that 4.5% of the total O present was in the O\(^2\) state (see Table 4). Using the O/Cr ratio for Cr\(_2\)O\(_3\) (1.5), the corresponding Cr\(^{3+}\) contribution to the Cr 2p\(_{3/2}\) spectrum was estimated to be 13.7% and was modeled using the fits obtained from analysis of the polycrystalline powder sample Cr\(_2\)O\(_3\)-2 (see Table 3). After constraining the area of the Cr\(_2\)O\(_3\) component to those in the other major crystallographic orientations (grey lines) [24]. The spectrum for a polycrystalline powder would be expected to be somewhat broadened by the presence of the oxide in orientations each with its own particular BE; and this could be one of several reasons for the broadening observed in the 2p spectra of many metal oxides. Although spectral broadening due to differential surface charging cannot be completely ruled out, any charging effects are thought to be small due to the use of a charge neutraliser during XPS analysis and the fact that the samples were pressed into a non-conducting polyethylene tape. Thus, this work has served to better define the Cr 2p\(_{3/2}\) and O 1s line shapes and positions for differing orientations of Cr\(_2\)O\(_3\), as well as show that an O/Cr ratio for the appropriate peaks mirrors that for the known stoichiometry.

### 3.2. Spectral refinements for Cr(OH)\(_3\)

The XPS spectra collected from a hydrated Cr(OH)\(_3\)\(_\times\)H\(_2\)O powder presented in an earlier publication (see Fig. 4 in Ref. [11]) has been re-analysed here. In the original analysis it was determined that a small Cr\(_2\)O\(_3\) impurity was present [11]. Refitting of the O 1s spectrum (see Fig. 5(a)) showed a small O\(^2\) component at 529.7 eV, a large peak representing the overlapping signal from substitutional OH\(^-\) and adsorbed organic species at 531.6 eV, and a third peak attributed to H\(_2\)O of hydration at 533.5 eV (see Table 4). From the O 1s analysis it was determined that 4.5% of the total O present was in the O\(^2\) state (see Table 4). Using the O/Cr ratio for Cr\(_2\)O\(_3\) (1.5), the corresponding Cr\(^{3+}\) contribution to the Cr 2p\(_{3/2}\) spectrum was estimated to be 13.7% and was modeled using the fits obtained from analysis of the polycrystalline powder sample Cr\(_2\)O\(_3\)-2 (see Table 3). After constraining the area of the Cr\(_2\)O\(_3\) component to

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**Table 5**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Normalised surface concentration (at.%)</th>
<th><strong>O(^2)</strong> or OH(^-)</th>
<th>Cr metal</th>
<th>Oxidized Cr</th>
<th>O/Cr</th>
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</thead>
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<td>Cr(_2)O(_3)-1</td>
<td>33.9</td>
<td>23.3</td>
<td>1.5</td>
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<td>Cr(_2)O(_3)-2</td>
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<td>Cr(_2)O(_3)-4</td>
<td>37.1</td>
<td>22.9</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(OH)(<em>3)(</em>\times)H(_2)O oxide</td>
<td>13.3</td>
<td>0.9</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The hydroxide surface concentration was calculated using the organic subtracted OH\(^-\) peak area from Table 4.
3.3. Reactions of metallic Cr with O2 and H2O

Clean polycrystalline Cr metal surfaces were exposed to ultra pure O2 gas for doses of 6.0 × 10^8 and 2.4 × 10^8 L at 300 °C and a pressure of 1 Torr. Two additional metal samples were exposed to a 3.0 × 10^8 L dose of H2O vapour under the same temperature and pressure conditions. Representative Cr 2p3/2 spectra produced by reactions with O2 gas for a dose of 2.4 × 10^8 L and H2O vapour for a dose of 3.0 × 10^8 L are shown in Fig. 6(a) and (b). A strong metal signal at 573.6 ± 0.1 eV was observed on all surfaces indicating the formation of thin oxide films. Fitting of the Cr 2p3/2 spectra shown in Fig. 6(a) and (b) was undertaken to separate the metallic contributions from those of the oxide. The metal portion of each spectrum was fit using the metal components presented in Table 3. The remaining spectral intensity was then assigned to the oxide component. The corresponding O 1s spectra (see Fig. 6(c) and (d)) were fit with an O2− component at 530.1 ± 0.1 eV and a peak attributed to adsorbed surface species at 531.7 ± 0.2 eV (see Table 2). The O/Cr ratios were calculated using the corrected O2− and non-metallic Cr surface intensities and found to be 1.7 for all samples (see Table 5). This result suggests that these films are deficient in Cr3+ and is supported by the low temperature oxidation mechanism first presented by Cabrera and Mott for p-type transition metal oxides [1–5]. In the case of Cr metal, the oxidation reaction involves the formation of Cr3+ vacancies at the oxide/gas interface. Over time there is an inward migration of these vacancies towards the metal substrate in an electric field set up by electrons tunnelling through the oxide film. At the same time metallic Cr atoms are oxidised at the metal/oxide interface and travel through these vacancy sites as well as grain boundaries to the oxide/gas interface, where they react with either O2 or H2O promoting further film growth [1–5].

To better observe the structure of the oxidised Cr species, the metal peak was removed and the resultant subtracted spectra are shown in Fig. 6(e) and (f). After spectral subtraction the oxide components were cleanly separated. These spectra were then fit with the line shape obtained previously for the polycrystalline Cr2O3 powder (Cr2O3-2 from Table 3). Most of the envelope was well fit with the line shape for Cr2O3; however additional contributions to the reaction spectra were clearly detected at the low BE side of the Cr2O3 envelopes. We attribute this to a hypo-stoichiometric CrO3 (Cr2O3−x) component that is likely formed during the initial stages of the reaction. To our knowledge this species has not been observed previously using XPS; its presence is somewhat comparable to the formation of Ni3+ during initial oxidation of Ni metal [14,15]. The exact nature of this Cr species is not identified here as there was no model structure available. However, in a previous study on the oxidation of Cr metal, it was suggested that film growth proceeded through the formation of Cr3+ and O2− vacancies [6,25]. Both of these vacancies are said to carry a negative charge and to maintain charge balance, Cr2+ cations are created and are situated in the interstitial sites of the Cr2O3 film [6,25]. The subtracted Cr 2p3/2 spectra collected from the H2O dosed surfaces showed the largest contributions from the hypo-stoichiometric component relative to the regular Cr2O3. This is probably the result of the thin nature of these films, as the sub-stoichiometric component would comprise a larger portion of the oxide. However, it is also possible that incorporation of other species such as H, a product of the dissociation of H2O.
The high-resolution Cr 2p$_{3/2}$ spectra collected from metal surfaces following doses of (a) $2.4 \times 10^8$ L of O$_2$ gas and (b) $3.0 \times 10^8$ L of H$_2$O vapour at 300 °C and 1 Torr. The O 1s spectra for the (c) $2.4 \times 10^8$ L of O$_2$ gas and (d) $3.0 \times 10^8$ L of H$_2$O vapour are also shown. The metal component was removed from each Cr 2p$_{3/2}$ spectrum and the resultant subtracted spectra for doses of (e) $2.4 \times 10^8$ L of O$_2$ gas and (f) $3.0 \times 10^8$ L dose of H$_2$O vapour are also presented. The subtracted spectra show the possible presence of a hypo-stoichiometric Cr$_2$O$_3$ oxide.

The high BE peak found near 531.7 ± 0.2 eV in the O 1s spectra has a similar chemical shift to that of OH$^-$ (see Table 4) however, the presence of significant levels of Cr(OH)$_3$ on any of the oxidised surfaces is unlikely on the basis of the observed O/Cr ratios. From the analysis of the accompanying C 1s spectra it was determined that a significant amount of the intensity of the high BE O 1s peak results from the presence of adsorbed organic species (see Tables 2 and 4). It is believed that the remaining intensity would result from the presence of adsorbed O and/or OH species, which are possible intermediates in the oxidation reaction [5].
Fig. 7. The high-resolution (a) Cr 2p3/2 spectrum from a Ni–Cr (20%) alloy surface containing a mixture of Cr2O3 (black lines) and Cr(OH)3 (grey lines). The corresponding (b) Ni 2p3/2 and (c) O 1s spectra are also shown.

3.4. Aqueous reaction of metallic Ni–Cr (20%)

Fig. 7(a) contains the Cr 2p3/2 high-resolution spectra collected from a Ni–Cr (20%) alloy electrochemically oxidised at 150 °C for a 72 h period at a pH of 5. The spectrum was fit with contributions from the polycrystalline Cr2O3 (black lines, Cr2O3-2) and Cr(OH)3 (grey lines) powders presented in Table 3, and a good fit of the envelope was observed. A small O2− peak in the O 1s spectrum at 529.6 eV was observed and verified the presence of Cr2O3 (see Fig. 7(c)). None of the O2− signal could be attributed to NiO, as the analysis of the Ni 2p3/2 spectrum (see Fig. 7(b)) showed all oxidised Ni species were present as Ni(OH)2. The Ni 2p3/2 spectrum was fit using the components for Ni(OH)2 presented in a previous publication [18]. There was no spectral evidence to suggest that a sub-stoichiometric Cr species formed under these oxidation conditions.

4. Conclusions

The Cr 2p3/2 spectra collected from samples of polycrystalline Cr2O3 powder were found to exhibit a multiplet structure very similar to that predicted by Gupta and Sen for the free Cr3+ ion. The narrowest Cr 2p3/2 spectra were obtained following annealing of fractured surfaces to 550 °C. Heating of the samples is believed to result in conversion of polycrystalline surface structures to a single (0 0 0 1) orientation having a slightly different BE than that for the polycrystalline surface. A small separation in BE was observed between the Cr3+ atoms oriented in the (0 0 0 1) direction relative to those found in the other major crystallographic arrangements. Additionally, a possible line shape for the Cr 2p3/2 spectrum for Cr(OH)3 was modeled using synthetic components from a sample containing contributions from both Cr2O3 and Cr(OH)3.

Analysis of the Cr 2p3/2 spectra collected from metallic Cr surfaces exposed to both O2 gas and H2O vapour showed the formation of thin Cr3+ deficient Cr2O3 films with a contribution from a hypo-stoichiometric component (Cr(2+8)O3−3). The concentration of this Cr species was found to be greater on the surfaces exposed to H2O vapour. No Cr(OH)3 appears to form following exposure to H2O vapour. A different result was observed following the aqueous oxidation of a Ni–Cr (20%) alloy, with contributions from both Cr2O3 and Cr(OH)3 observed in the Cr 2p3/2 spectrum. There was no spectral evidence to suggest the formation of a hypo-stoichiometric Cr species.

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References