Hard X-ray Photoelectron Spectroscopy (HAXPES) characterisation of electrochemical passivation oxide layers on Al–Cr–Fe complex metallic alloys (CMAs)

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http://dx.doi.org/10.1016/j.elecom.2014.05.024
1388-2481/© 2014 Published by Elsevier B.V.

1. Introduction

Al–Cr–Fe complex metallic alloys (CMAs) are intermetallic phases occurring as crystalline approximants of quasicrystals [1,2] and present peculiar bulk [3] and surface properties, such as low friction, hydrophobicity and high corrosion resistance in the 0–14 pH range [4,5], being good candidates as multifunctional corrosion protecting coatings. Their corrosion resistance in very aggressive environments, such as acidic sulphuric or chloride containing electrolytes, has been proven by electrochemical techniques [4,5]. The formation of a 6–8 nm thick protective passive layer composed of several Al and Cr oxyhydroxide stacks was evidenced by X-ray Photoelectron Spectroscopy (XPS) [4,6] and complementary XPS and Auger sputtering depth profile analyses, which are typically used to determine the depth-resolved chemical constitution of layers with a thickness exceeding the XPS information depth. However, the main disadvantages of the latter techniques are the possible preferential sputtering effects and the need for an accurate calibration of the sputtering rate [7]. Investigation of the oxidation mechanism not only requires detailed information on the oxide constitution, but also on the oxidation-induced changes in the alloy adjacent to the alloy/oxide interface [8]. Unfortunately, the information depth obtained by angle-resolved XPS analysis using a conventional Al- or Mg-X-ray source is limited to about 6 nm and therefore cannot probe the alloy/oxide interface for ‘thicker’ passive oxide layers, as formed by e.g. electrochemical polarisation [10]. Furthermore, the energy resolution of standard laboratory setups is typically insufficient to unequivocally resolve the oxide and hydroxide components in measured core-level spectra of oxidised alloys [9].

The present study demonstrates that Hard X-ray XPS (HAXPES) is a very powerful technique to characterise relatively thick, multi-element...
oxyhydroxide layers on Al–Cr–Fe CMAs as formed by potentiostatic anodic polarisation. By tuning the energy of the incident X-rays up to 10 keV [10,11], HAXPES can effectively probe the chemical constitution as a function of depth over the entire passive layer and across the reacting alloy/oxide interface. In addition, the use of a synchrotron source with monochromatised X-ray optics provides an enhanced energy resolution as compared to conventional setups, thus allowing simultaneous analysis of shallow and deep core-level photoelectron lines (like Al 2s and Al 1s), thereby opening the field to new physics. As demonstrated in this work, the use of high-energy resolution at various excitation energies is essential for identifying the chemical environments in the multi-element oxyhydroxide layers formed by electrochemical treatments for which a direct comparison with known reference oxide and/or hydroxide bulk compounds is not possible.

2. Experimental Details

2.1. Materials and Electrochemical Treatment

Four Al-based CMA intermetallics; the orthorhombic Al78.8Cr15.5Fe5.7 and Al79.1Cr17.8Fe3.1, the hexagonal Al78.7Cr20.6Fe0.7 and the cubic Al64.2Cr27.2Fe8.1 (at.%) phases were investigated. Corresponding single crystals were prepared at LMU (Munich) [12]. The polycrystalline cubic phase was prepared at Institut Jean Lamour (Nancy). All the samples were polished to mirror finish using diamond paste and ethanol and electrochemically anodically potentiostatic polarised in the low passive domain at 0 V SCE for 24 h in sulphuric acid electrolytes at pH 0 or 1, using a conventional three electrode cell.

2.2. HAXPES Measurements

The measurements were conducted at the ID32 beamline of the ESRF. The excitation energy was varied from 2.3 to 10.0 keV. A double-crystal Si(111) monochromator and a PHOIBOS 225 HV hemispherical electron analyser [13] were used to record HAXPES spectra at various photoelectron take-off angles. High-resolution measurements were performed using additional Si(333) and Si(555) post-monochromators. The binding energy (BE) was calibrated using gold. CasaXPS (2009 Casa Software Ltd) was used for data analysis, applying a Shirley-type background and asymmetric lineshapes for the metallic peaks and symmetric Gaussian/Lorentzian lineshapes for the oxidic ones (see Appendix A for details). The lineshapes of the metallic peak components were determined from the spectra of clean alloys. Due to the variation of the energy resolution with the excitation energy

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Fig. 1. Reconstructed high-resolution Al 2s, Al 1s and Cr 2p_{3/2} spectra for the Al78.7Cr20.6Fe0.7 alloy after metallographic polishing without (a,c) and with (b,d) sputter/annealing and subsequent electrochemical polarisation in sulphuric acid (pH 1) for 24 h at 0 V SCE, as recorded at 6 and 10 keV, respectively.
(different source/analyser resolution, use of post-monochromators), the lineshape parameters can be different for different excitation energies.

3. Results and Discussion

Fig. 1 displays exemplary Al 2s, Al 1s and Cr 2p3/2 spectra recorded at 6.0 and 10.0 keV for the Al78.7Cr20.6Fe0.7 alloy after two different surface treatments, but identical electrochemical potentiostatic polarisations in sulphuric acid at pH 1: see caption for details. For all specimens studied, no oxidised state of Fe could be detected in the Fe 2p3/2 core-level spectra, indicating that Fe does not contribute to the formation of the passivation layer.

At least two oxidic components were identified in the Al 2s spectra positioned at shifts of +1.7 and +2.7 (±0.1) eV with respect to the metallic peak, as attributed to Al-oxide-like and Al-hydroxide-like environments, respectively. Such components were also identified in the Al 1s spectra at relative chemical shifts of +1.6 and +2.5 (±0.1) eV.

Fig. 1a,b shows that the Al 1s core-level, as positioned at much higher BE, provides an enhanced surface sensitivity as compared to the Al 2s core level. Due to the enhanced degree of hydroxylation near the surface, the Al 1s spectra thus show a more pronounced contribution of the Al-hydroxide component. The Cr 2p3/2 oxidic spectra (Fig. 1c,d) can also be described by at least one oxide-like and one hydroxide-like component with a respective chemical shift of +2.5 and +3.6 (±0.1) eV, in accordance with Ref. [14].

In summary, the HAXPES analysis evidences different local environments (i.e. oxide and hydroxide) for the Al and Cr cations in the defective oxyhydroxide layers formed on the Al–Cr–Fe complex metallic alloys after electrochemical treatment in sulphuric acid. The high degree of local disorder of the oxyhydroxide layers modifying the local coordination spheres around Al and Cr cations in the oxide- and hydroxide-like environments (e.g. bond lengths and angles, as well as ligand-type), results in relative large intrinsic widths and chemical shifts of the fitted oxide and hydroxide components.

Evaluation of the HAXPES spectra as a function of the excitation energy allowed a non-destructive, depth-resolved determination of the chemical constitution of the passivation layers. The Al 2s and Cr 2p3/2 spectra (Fig. 2, a–f) recorded at 2.3 keV and 3.8 keV for the Al64.2Cr27.2Fe8.1 alloy confirm the incorporation of both Al and Cr cations in the grown oxyhydroxide passivation layers with an enhanced degree of hydroxylation towards the outer surface. For low excitation energies
(i.e. more surface-sensitive), an additional minor component appears in the Al 2s and Cr 2p spectra, which is attributed to the residues of sulphate species from the electrolyte solution interacting with the passive layer outer surface. The O 1s core-level could not resolve the individual oxide and hydroxide components in the O 1s envelope in the presence of so different Al and Cr cations.

Passivation of the Al–Cr–Fe alloys is ensured by the formation of the (Al,Cr)–oxyhydroxide layer, as outlined above. The Cr oxide/Al oxide intensity ratios (summing the oxide and hydroxide components) evidence that the oxyhydroxide layers are richer in Cr cations towards their outer surface (Fig. 2g,h). The average thicknesses of the passivation layers formed by electrochemical polarisation of Al–Cr–Fe complex metallic alloys in very acidic electrolytes (sulphuric acid pH 1 or 0). Using Hard X-rays, deep core-level photoelectron lines which cannot be excited with conventional laboratory sources were collected (i.e. Al 1s). The shallow and deep core levels provided complementary information: i.e. the Al 1s signal allowed an enhanced surface sensitivity. Analysis and cross correlation of Al 1s, Al 2s, Cr 2p and O 1s spectra recorded at progressively increasing X-ray excitation energies (from 2.3 to 3.8 keV) and enhanced energy resolution revealed the distributions of Al and Cr cations in hydroxide-like and oxide-like local chemical environments as a function of depth below the surface and indicate a relative enrichment of Cr cations towards the outer passive layer surface.

Higher excitation energies (6–10 keV) were utilised to probe the interface (i.e. to record a reliable signal from the alloy substrate), thus allowing an estimation of the thickness of the passivation layers. As a final result, a Cr threshold of 18 at.% was identified, necessary for the formation of a thin protecting type passive oxyhydroxide layer on the Al–Cr–Fe complex metallic alloys.

### Table A1

Chemical assignment of the fitted components in the passivation layers on the Al$_{78.7}$Cr$_{20.6}$Fe$_{0.7}$ alloy after electrochemical treatment in sulphuric acid at pH 0 (excitation energy 2.3 keV, no post-monochromators used).

<table>
<thead>
<tr>
<th>Core level</th>
<th>Designation</th>
<th>BE (±0.1 eV)</th>
<th>PWHM (±0.1 eV)</th>
<th>Lineshape CasaXPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au 4f$_{7/2}$</td>
<td>Metal</td>
<td>84.0</td>
<td>0.6</td>
<td>A(0,1,0.400)[SGL(100)]</td>
</tr>
<tr>
<td>Al 2s</td>
<td>Metal</td>
<td>118.1</td>
<td>1.1</td>
<td>A(0.001,1.10)[SGL(80)]</td>
</tr>
<tr>
<td>Al 2s</td>
<td>Al oxide</td>
<td>119.8</td>
<td>1.6</td>
<td>SGL(30)</td>
</tr>
<tr>
<td>Al 2s</td>
<td>Al hydroxide</td>
<td>120.8</td>
<td>1.6</td>
<td>SGL(30)</td>
</tr>
<tr>
<td>Al 2s</td>
<td>Al sulphate</td>
<td>122.4</td>
<td>1.5</td>
<td>SGL(100)</td>
</tr>
<tr>
<td>Al 1s</td>
<td>Metal</td>
<td>1559.8</td>
<td>1.1</td>
<td>SGL(50)</td>
</tr>
<tr>
<td>Al 1s</td>
<td>Oxide</td>
<td>1561.4</td>
<td>1.7</td>
<td>SGL(30)</td>
</tr>
<tr>
<td>Al 1s</td>
<td>Hydroxide</td>
<td>1562.4</td>
<td>1.7</td>
<td>SGL(30)</td>
</tr>
<tr>
<td>Al 1s</td>
<td>Al sulphate</td>
<td>1564.5</td>
<td>1.8</td>
<td>SGL(50)</td>
</tr>
<tr>
<td>Cr 2p$_{3/2}$</td>
<td>Metal</td>
<td>574.0</td>
<td>1.2</td>
<td>A(0,0.40,0.5)[SGL(20)]</td>
</tr>
<tr>
<td>Cr 2p$_{3/2}$</td>
<td>Cr$_2$O$_3$</td>
<td>576.5</td>
<td>2.6</td>
<td>SGL(30)</td>
</tr>
<tr>
<td>Cr 2p$_{3/2}$</td>
<td>Cr(OH)$_3$</td>
<td>577.6</td>
<td>2.6</td>
<td>GL(30)</td>
</tr>
<tr>
<td>Cr 2p$_{3/2}$</td>
<td>CrO$_3$ or Cr sulphate</td>
<td>579.5</td>
<td>2.0</td>
<td>SGL(30)</td>
</tr>
<tr>
<td>Fe 2p$_{3/2}$</td>
<td>Metal</td>
<td>706.9</td>
<td>0.6</td>
<td>SGL(40)</td>
</tr>
<tr>
<td>O 1s</td>
<td>Cr oxide</td>
<td>531.5</td>
<td>1.5</td>
<td>GL(30)</td>
</tr>
<tr>
<td>O 1s</td>
<td>Al oxide and Cr hydroxide (overlapping)</td>
<td>532.7</td>
<td>2.2</td>
<td>SGL(20)</td>
</tr>
<tr>
<td>O 1s</td>
<td>Al hydroxide</td>
<td>534.5</td>
<td>1.5</td>
<td>SGL(30)</td>
</tr>
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</table>
References


