Influences of fluorine species on the anodizing behaviour of aluminium and AA 2024-T3 alloy

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<table>
<thead>
<tr>
<th>Table of content</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table of content</td>
<td>2</td>
</tr>
<tr>
<td>List of Tables</td>
<td>5</td>
</tr>
<tr>
<td>List of figures</td>
<td>8</td>
</tr>
<tr>
<td>Abbreviations</td>
<td>17</td>
</tr>
<tr>
<td>Abstract</td>
<td>18</td>
</tr>
<tr>
<td>Declaration</td>
<td>19</td>
</tr>
<tr>
<td>Copyright statement</td>
<td>20</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>21</td>
</tr>
<tr>
<td>The Author</td>
<td>23</td>
</tr>
<tr>
<td>1 Introduction</td>
<td>24</td>
</tr>
<tr>
<td>1.1 Aims of the project</td>
<td>25</td>
</tr>
<tr>
<td>1.2 Objectives of the project</td>
<td>25</td>
</tr>
<tr>
<td>1.3 The thesis structure</td>
<td>26</td>
</tr>
<tr>
<td>2 Literature review</td>
<td>27</td>
</tr>
<tr>
<td>2.1 Anodic films</td>
<td>27</td>
</tr>
<tr>
<td>2.1.1 DC anodizing</td>
<td>27</td>
</tr>
<tr>
<td>2.1.2 AC anodizing</td>
<td>28</td>
</tr>
<tr>
<td>2.2 Types of anodic films</td>
<td>28</td>
</tr>
<tr>
<td>2.2.1 Barrier-type films</td>
<td>29</td>
</tr>
<tr>
<td>2.2.2 Porous-type anodic oxide films</td>
<td>42</td>
</tr>
<tr>
<td>2.3 Aluminium alloy</td>
<td>57</td>
</tr>
<tr>
<td>2.4 Fluorine species in anodic films</td>
<td>61</td>
</tr>
<tr>
<td>3 Experimental work</td>
<td>63</td>
</tr>
<tr>
<td>3.1 Substrate Material</td>
<td>63</td>
</tr>
<tr>
<td>3.1.1 Aluminium</td>
<td>63</td>
</tr>
<tr>
<td>3.1.2 AA 2024-T3 alloy</td>
<td>63</td>
</tr>
<tr>
<td>3.2 Electrolyte preparation</td>
<td>63</td>
</tr>
<tr>
<td>3.2.1 Sulphuric acid</td>
<td>64</td>
</tr>
<tr>
<td>3.2.2 Tartaric/sulphuric acid (TSA)</td>
<td>64</td>
</tr>
</tbody>
</table>
3.2.3 Ammonium pentaborate ......................................................... 64
3.2.4 Fluoroacid additions ............................................................ 64
3.2.5 Sodium fluoride addition .................................................... 69
3.3 Anodic film formation ............................................................. 71
  3.3.1 Surface Pre-treatment .......................................................... 71
  3.3.2 Anodizing process .............................................................. 73
3.4 Anodic film examination .......................................................... 76
  3.4.1 Scanning electron microscopy .............................................. 76
  3.4.2 Transmission electron microscopy (TEM) .............................. 77
  3.4.3 Glow discharges optical emission spectrometer (GDOES) .......... 78
  3.4.4 Chemical dissolution of porous alumina films ......................... 79
  3.4.5 Porosity measurement ........................................................ 80
  3.4.6 Nuclear reaction analysis (NRA) .......................................... 80
  3.4.7 Rutherford backscattering spectroscopy (RBS) ....................... 81
  3.4.8 Nanoindentation hardness .................................................. 83
4 Effects of fluoride ions on the growth of barrier-type films on aluminium .......... 84
  4.1 Introduction ........................................................................... 84
  4.2 Results and Discussion .......................................................... 86
    4.2.1 The voltage-time curves .................................................. 87
    4.2.2 Transmission electron micrograph .................................... 88
    4.2.3 Compositional analysis of films by EDX spectroscopy .......... 90
    4.2.4 Elemental depth profiles by Glow Discharge Optical Emission Spectrometer (GDOES) ................................................................. 92
    4.2.5 Scanning electron microscopy .......................................... 96
  4.3 Conclusions ........................................................................... 98
5 Influence of fluorozirconic acid on sulphuric acid anodizing of aluminium ............ 99
  5.1 Introduction ........................................................................... 99
  5.2 Results and Discussion .......................................................... 100
    5.2.1 Current density-time curves and film morphologies ............. 100
    5.2.2 Film compositions: EDX spectroscopy ............................... 106
    5.2.3 Film compositions: GDOES .............................................. 109
### List of Tables

Table 3-1 Amount of free and bonded fluoride, determined using a silicon/platinum electrode cell, (1<sup>st</sup> row) before precipitation, after precipitation of the free fluoride (2<sup>nd</sup> and 4<sup>th</sup> rows) and after precipitation of the attached fluoride (3<sup>rd</sup> row).......................................................... 66

Table 3-2 Amount of free fluoride in the fluoroacids, derived from the results presented in Table 3.1. ........................................................................................................................................ 67

Table 3-3. Free fluoride in the electrolyte solution of 0.1 M sulphuric acid mixed with fluoroacids. .......................................................................................................................... 70

Table 4-1 Results of EDX analyses of films formed at 5 mA cm<sup>2</sup> in 0.1 M ammonium pentaborate solution containing sodium fluoride at 20 °C.................................................. 91

Table 5-1. Concentrations of fluorozirconic acid (FZ), total fluorine and free fluoride added to 0.1 M sulphuric acid electrolyte. .......................................................................................................................... 100

Table 5-2. Thicknesses of films, determined by SEM, and charge density passed for anodizing of aluminium for 1200 s at 22 V in 0.1 M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of fluorozirconic acid (FZ) at 0 °C and 20 °C. The thicknesses in bold type indicate a collapsed porous structure at the film surface. ........................................................................... 104

Table 5-3. Thicknesses of films and charge density passed for anodizing of aluminium at 22 V for 1200 s in 0.1 M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of sodium fluoride at 0 °C and 20 °C. The thickness value in bold type is a film with a collapsed porous structure at the film surface. No measurements were made for 3.5 x 10<sup>-1</sup> M NaF at 20 °C due to severe film dissolution. ........................................................................................................ 105

Table 5-4. EDX analyses of anodic films formed on aluminium for 300 s at 22 V in 0.1 M H<sub>2</sub>SO<sub>4</sub> or 1.0 M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of fluorozirconic acid (FZ) or
sodium fluoride at 0 °C and 20 °C. (n.d.= not determined due to low kV required for analysis)........................................................................................................................................................................107

Table 5-5. EDX analyses of a cross-section of an anodic film formed on aluminium for 1200 s at 22 V in 0.1 M H$_2$SO$_4$ containing 1.0 wt.% fluorozirconic acid 20 °C. ................................................................. 111

Table 5-6. Dissolution rates of the barrier layer in 0.1 M sulphuric acid containing either 0.1 or 1.0 wt.% fluorozirconic acid (FZ) at 0 and 20 °C. ............................................................................................. 113

Table 5-7. Porosities of films formed on aluminium for 1200 s at 22 V in 0.1 M H$_2$SO$_4$ containing 0, 0.1, 0.5 and 1.0 wt.% fluorozirconic acid (FZ) at 0 and 20 °C. ................................................................. 115

Table 6-1. Concentrations of fluoroacids, total fluorine and free fluoride added to 0.1 M sulphuric acid electrolyte. ........................................................................................................................................... 124

Table 6-2. Thicknesses of films, determined by SEM, and charge density passed for anodizing of AA 2024-T3 alloy for 1200 s at 22 V in 0.1 and 1.0 M H$_2$SO$_4$, without (control) and with the addition of 0.1 wt.% fluorozirconic acid at 0 and 20 °C. ................................................................. 125

Table 6-3. Thicknesses of films, determined by SEM, the charge density passed and the ratio of the thickness to the charge for anodizing of aluminium and AA 2024-T3 alloy in 0.53 M tartaric acid/0.4 M sulphuric acid without (control) and with addition of 0.1 wt.% fluorozirconic acid, at 0, 20 and 37 °C. The anodizing was carried out by their stepping the voltage to 14 or 18 V, or under a constant voltage of 18 V. ................................................................. 141

Table 7-1. Concentrations of fluoroacid and free fluoride added to 0.1 M sulphuric acid electrolytes. ...................................................................................................................................................... 148

Table 7-2. Thicknesses of films, determined by SEM, and charge density passed for anodizing of aluminium and AA 2024-T3 alloy for 1200 s at 22 V in 0.1 containing 0.1 wt.% fluoroacids at 0 °C and 20 °C. The thickness values in bold type are for films with a collapsed porous structure at the film surface. ....................................................................................... 153
Table 7-3. Results of EDX analyses of anodic films formed on aluminium for 300 s at 22 V in 0.1 M H₂SO₄ containing different concentrations of fluoroacids or sodium fluoride at 0 °C and 20 °C. ........................................................................................................................................................................ 154

Table 7-4. Results of hardness measurements made on aluminium anodized for 1200, 2400 and 7200 s, in 0.1 M sulphuric acid containing 0.1 wt.% fluoroacid at 0 °C. .......................... 158
List of figures

Figure 2-1. Schematic illustration of the cross sections of anodic films on aluminium: (a) barrier-type film, (b) porous anodic film, revealing the barrier layer, pores and cells [44] . 29

Figure 2-2  Schematic illustrations of ultramicrotomed sections of various kinds of barrier-type films formed on aluminium. (a) The relatively uniform thickness and textureless on initial examination. (b) Location of a xenon marker, which is directly visible in TEM as fine bubbles in the film sections. The xenon is found at a depth of about 0.4 of the total barrier layer film thickness measured from the film surface. (c) Section of the barrier film created in aqueous borate solution and subsequently exposed to the electron beam to induce crystallization of the interior film region. The crystallized inner film region extends from the metal/film interface to the position of the xenon marker revealed in (b), which indicates that boron species are immobile. (d) Section of the film formed in phosphate solution and afterwards exposed to the electron beam to induce crystallization of the internal film region. The crystallized internal film region extends to 0.3 of the full film thickness from the metal/film interface and does not reach the marker layer; this indicates that incorporated phosphate species are mobile inwards. (e) Section of the film formed in molybdate solution, with the exterior molybdenum-containing layer revealed by an atomic number contrast effect. (f) Section of molybdate film exposed to the electron beam. Subsequent crystallization extends to the external region containing incorporated anions and indicates that the molybdenum species are mobile outwards [35].................. 36

Figure 2-3  Schematic diagram showing Al³⁺ egress and O²⁻/OH⁻ ingress under an electric field [98]............................................................. 38

Figure 2-4  Schematic diagram showing the formation of a barrier type anodic alumina film on high purity aluminium, at high efficiency [100]................................................... 39

Figure 2-5  Schematic diagram showing anodic film formation on high-purity aluminium, (a) Constant current anodizing, (b) Constant voltage anodizing [121]............................... 44
Figure 2-6  Schematic representation of a porous anodic film showing the principal morphological features [45].

Figure 2-7  Schematic illustrations of ultramicrotomed sections of anodic films corresponding to the introductory stages of pore development: (a) introductory growth of a relatively uniform alumina during the rising voltage region; (b) subsequent development of penetration paths into the alumina; (c) further development of penetration paths with a preferred development of the embryo pores and regions of disaggregated alumina at the film/electrolyte interface [98].

Figure 2-8. Schematic diagram showing the distribution of a tungsten tracer in anodic films. (a) pre-anodized aluminium substrate with barrier layer. (b) sputtering-deposited aluminium with a tungsten tracer, (c) the tracer layer following incorporation into a barrier film. (d) The distorted tracer layer following incorporation into the barrier layer region of a porous anodic film. The distortion arises from flow of alumina material from the barrier layer at the base of the porous toward the cell walls. The material flow proceeds as the anodizing time increase as shown in (e) and (f) [129].

Figure 2-9. Schematic diagram illustrating qualitatively the differing behaviour of tungsten species incorporated into porous anodic films formed in (a) sulphuric acid and (b) borax. The diagrams show the progress of the tungsten species (dark band) through the barrier layer beneath a pore with increase of anodizing time. (a) Showing field-assisted flow of oxide (flow model). (b) Showing field-assisted dissolution (dissolution model) [145].

Figure 2-10 Schematic diagrams showing the plan and cross section for the major anodizing acids: (a) sulphuric; (b) oxalic; (c) phosphoric; (d) chromic acid. The cell comprises acid anion contaminated film material next to the pore and relatively pure alumina where cells meet [149].

Figure 2-11  Distribution of the voltage drop and field (the slope of the voltage-distance plot) across typical barrier layers of porous anodic films formed in each of the major acids: a) sulphuric acid, b) oxalic acid, c) phosphoric acid, d) chromic acid [149].

Figure 3-1, Schematic diagram showing the electropolishing apparatus.
Figure 3-2. Schematic diagrams showing aluminium and AA 2024-T3 alloy specimens. The specimens were completely coated on one side and partly coated on the other side using an insulating lacquer. ............................................................................................................................... 73

Figure 3-3. Schematic diagram of the anodizing process. ................................................................................................. 74

Figure 3-4. Schematic diagram shown step anodizing procedure [185] .............................................................................. 75

Figure 3-5. Origin and information depth of secondary electrons (SE), backscattered electrons (BSE), Auger electrons (AE) and X-ray quanta (X) in the diffusion cloud of electron range R for normal incidence of the primary electrons (PE) [186]. ........................................................................... 76

Figure 3-6. (a) Photograph of Zeiss Ultra 55 FEG-SEM and (b) schematic of the column of a standard instrument showing the main components [187]. ....................................................................................... 77

Figure 3-7. (a) Photograph of FEI-Philips CM20 and (b) schematic of the TEM column showing the main components [187]. .................................................................................................................. 78

Figure 3-8. (a) Schematic diagram of analysis of specimens using nuclear reaction analysis. (b) The principle of analysis of specimens using nuclear reaction analysis; the incident beam strikes the surface of the tested specimen and (c) an emitted particle from the nuclear reaction is detected with a given angle [193]. ....................................................................................... 82

Figure 3-9. Schematic diagram of analysis of specimens using Rutherford backscattering spectrometry; the incident beam strikes the surface on the test specimen and is backscattered with a given angle [191]. ................................................................................................. 83

Figure 4-1. Voltage-time curves for aluminium specimens anodized at 5 mA cm\(^{-2}\) in 0.1 M ammonium pentaborate solution at 20 °C, with various additions of sodium fluoride. (a) A. No addition. B 3.5 \times 10^{-4} \text{ M NaF. C} 3.5 \times 10^{-3} \text{ M NaF. D} 3.5 \times 10^{-2} \text{ M NaF.} (b) E 3.5 \times 10^{-1} \text{ M NaF.} .......................................................................................................................... 86

Figure 4-2 Voltage-time curves for an aluminium specimen anodized in two stages at 5 mA cm\(^{-2}\) in 0.1 M ammonium pentaborate solution containing 3.5 \times 10^{-2} \text{ M NaF at 20 °C. After anodizing to 100 V in the first stage, the specimen was left in the electrolyte for}
The second stage of anodizing was then started and continued until the voltage reached 200 V.

Figure 4-3 Transmission electron micrograph (HAADF image) and EDX elemental maps of oxygen, aluminium and fluorine for an aluminium specimen that had been anodized to 100 V at 5 mA cm\(^{-2}\) in 0.1 M ammonium pentaborate solution containing 3.5 x 10\(^{-2}\) M NaF at 20 °C.

Figure 4-4 EDX spectra for aluminium specimens that had been anodized at 5 mA cm\(^{-2}\) and 20 °C in 0.1 M ammonium pentaborate solution containing (a) 3.5 x 10\(^{-4}\) M NaF to 100 V, (b) 3.5 x 10\(^{-3}\) M NaF to 100 V, (c) 3.5 x 10\(^{-2}\) M NaF to 100 V and (d) 3.5 x 10\(^{-2}\) M NaF to 200 V.

Figure 4-5 GDOES elemental depth profiles for aluminium specimens anodized at 5 mA cm\(^{-2}\) in 0.1 M ammonium pentaborate solution at 20 °C (a) to 100 V with no addition of NaF; (b) to 100 V with addition of 3.5 x 10\(^{-2}\) M NaF; (c) to 200 V with addition of 3.5 x 10\(^{-2}\) M NaF; (d) to 100 V with no addition of NaF followed by to 200 V with addition of 3.5 x 10\(^{-2}\) M NaF. The aluminium, oxygen, boron and fluorine intensities were multiplied by factors of 5, 10, 10 and 1 respectively.

Figure 4-6 Schematic diagram showing (a) the film formed to 100 V in ammonium pentaborate solution and (b) the film formed by further anodizing to 200 V in ammonium pentaborate solution containing 3.5 x 10\(^{-2}\) M NaF.

Figure 4-7 Scanning electron micrographs of the surface of an aluminium specimen that had been anodized for 600 s at 5 mA cm\(^{-2}\) in 0.1 M ammonium pentaborate solution, containing 3.5 x 10\(^{-2}\) M NaF, at 20 °C. (a) General view of the surface. (b,c) Increased magnification images of regions in (a). (d) Cross-section of the specimen.

Figure 5-1. Current-density-time curves for aluminium anodized at 22 V in 0.1 M H\(_2\)SO\(_4\) at (a) 0 °C and (b) 20 °C. Curves A and E – control specimens anodized without fluorozirconic acid; curves B and F – 0.1 wt.% fluorozirconic acid; curves C and G – 0.5 wt.% fluorozirconic acid; curves D and H – 1.0 wt.% fluorozirconic acid. (c) Anodized in 1.0 M H\(_2\)SO\(_4\); curves A and C – control specimens anodized without fluorozirconic acid at 0 °C.
and 20 °C, respectively; curves B and D – 0.1 wt.% fluorozirconic acid at 0 and 20 °C, respectively. 

Figure 5-2. Scanning electron micrographs (backscattered electrons) of the surfaces of anodic films formed on aluminium at 22 V in 0.1 M H₂SO₄ at 0 °C (top row) and at 20 °C (bottom row). A and E – control specimens anodized without fluorozirconic acid; B and F – 0.1 wt.% fluorozirconic acid; C and G – 0.5 wt.% fluorozirconic acid; D and H – 1.0 wt.% fluorozirconic acid.

Figure 5-3. Scanning electron micrographs (secondary electron electrons) of the cross-sections of anodic films formed on aluminium at 22 V in 0.1 M H₂SO₄ at 0 °C (top row) and at 20 °C (bottom row). A and E – control specimens anodized without fluorozirconic acid; B and F – 0.1 wt.% fluorozirconic acid; C and G – 0.5 wt.% fluorozirconic acid; D and H – 1.0 wt.% fluorozirconic acid.

Figure 5-4. Bright-field transmission electron micrographs of ultramicrotomed cross-sections of aluminium anodized at 22 V for (a) 300 s, and (b) 1200 s, in 0.1 M H₂SO₄ containing 0.1 wt.% fluorozirconic acid at 0 °C.

Figure 5-5. Relationship between the F: Al atomic ratio in the film and the average current density during anodizing of aluminium at 22 V for 300 s, in 0.1 M H₂SO₄ containing either fluorozirconic acid (FZ) or sodium fluoride (NaF) additions at 0 and 20 °C. The F:Al ratios are taken from Table 4 for specimens anodized with 0.1, 0.5 and 1.0 wt.% fluorozirconic acid and with 3.5 x 10⁻³, 3.5 x 10⁻² and 3.5 x 10⁻¹ M sodium fluoride. (▲ FZ 20 °C, ■ FZ 0 °C, ● NaF 20 °C, ★ NaF 0 °C).

Figure 5-6. GDOES elemental profiles of aluminium anodized at 22 V for 300 s in 0.1 M H₂SO₄ at 0 °C containing (a) 0.1, (b) 0.5 and (c) 1.0 wt.% fluorozirconic acid. The aluminium, oxygen, boron and fluorine intensities were multiplied by factors of 5, 10, 10 and 1 respectively.

Figure 5-7. Experimental and simulated (solid line) RBS spectra for aluminium anodized at 0 °C in 0.1 M H₂SO₄ containing 0.1 wt.% fluorozirconic acid.
Figure 5-8 Relationship between the barrier layer thickness and the time of immersion in 0.1 M H₂SO₄ with addition of (a) 0.1 % fluorozirconic acid at 0 °C; (b) 0.1 % fluorozirconic acid at 20 °C; (c) 1.0 % fluorozirconic acid at 0 °C; 1.0 % fluorozirconic acid at 20 °C. Each specimen was first anodized at 22 V in the same electrolyte for 1200 s. .................. 114

Figure 5-9. Schematic diagram showing the proposed distribution of species in films formed in sulphuric acid containing fluorozirconic acid........................................................ 118

Figure 6-1. Current-density-time curves for AA2024-T3 alloy anodized at 22 V at 0 °C and 20 °C in (a) 0.1 M H₂SO₄ and (b) in 1 M H₂SO₄. Curves A and D – control specimens anodized without fluorozirconic acid; curves B and E – 0.1 wt.% fluorozirconic acid; curves C and F – 0.5 wt.% fluorozirconic acid, at 0 and 20 °C, respectively. .................. 123

Figure 6-2. Scanning electron micrographs (secondary electrons) of the surfaces (1st column) and cross-section (2nd column) of anodic films formed by anodizing AA 2024 alloy in 0.1 M sulphuric acid at 22 V at 0 °C for 1200 s; A – control; B - with 0.1% fluorozirconic acid and C- with 0.5% fluorozirconic acid. .................................................................................. 124

Figure 6-3. Current-density-time curves for (a) aluminium and (b) AA 2024 alloy anodized to 14 V in 0.53 M tartaric /0.4 M sulphuric acid without and with 0.1 wt.% fluorozirconic acid. Curves A, B and C – control specimens anodized without fluorozirconic acid; curves D, E and F – 0.1 wt.% fluorozirconic acid, at 0, 20 and 37 °C, respectively. .................. 129

Figure 6-4. Current-density-time curves for (a) aluminium and (b) AA 2024 alloy anodized to 18 V in 0.53 M tartaric /0.4 M sulphuric acid without and with 0.1 wt.% fluorozirconic acid. Curves A, B and C – control specimens anodized without fluorozirconic acid; curves D, E and F – 0.1 wt.% fluorozirconic acid, at 0, 20 and 37 °C, respectively. .................. 130

Figure 6-5. Current-density-time curves for (a) aluminium and (b) AA 2024 alloy anodized at 18 V in 0.4 M sulphuric/ 0.53 tartaric acid without and with 0.1 wt.% fluorozirconic acid. Curves A and B – control specimens anodized without fluorozirconic acid; curves C and D – 0.1 wt.% fluorozirconic acid, at 0 and 20 °C, respectively.............................................. 131
Figure 6-6. Scanning electron micrographs (secondary electrons) of the surfaces of anodic films formed on aluminium (1st column - control and 2nd column - with 0.1% fluorozirconic acid) and on AA 2024-T3 alloy (3rd column- control and 4th column - with 0.1% fluorozirconic acid) to 18 V in 0.53 M tartaric /0.4 M sulphuric acid at 0, 20 and 37 °C. ........................................................................................................................................................................132

Figure 6-7. Dependence of the growth rates of the films on (a) aluminium and (b) AA 2024-T3 alloy on temperature; ★ specimens anodized in TSA up to 14 V; ■ specimens anodized in TSA up to 18 V; ● specimens anodized in TSA with 0.1 % fluorozirconic acid up to 14 V; ▼ specimens anodized in TSA with 0.1 % fluorozirconic acid up to 18 V.............136

Figure 6-8. Current-density-time curves for aluminium anodized to 14 V in 0.53 M tartaric /0.4 M sulphuric acid without fluorozirconic acid, curves A, B and C, and with 0.5wt.% fluorozirconic acid, curves D, E and F, at 0, 20 and 37 °C. .............................................................................137

Figure 6-9. Scanning electron micrographs (secondary electrons) of cross-sections of anodic films formed by anodizing aluminium to 14 V for 1560 s in 0.53 M tartaric / 0.4 M sulphuric acid; 1st row anodized at 0 °C; 2nd row anodized at 20 °C; 3rd row anodized at 37 °C; A, B and C – control specimens; D, E and F - with 0.1% fluorozirconic acid and G, H and I- with 0.5% fluorozirconic acid. ......................................................................................................................138

Figure 6-10. Thickness of films formed on aluminium following anodizing at 14 V for 1560 s in 0.4 M sulphuric/ 0.53 tartaric acid with different FZ addition at ■ 0 °C, ● 20 °C, ▲ 37 °C. ..................................................................................................................................................139

Figure 7-1. Current-density-time curves for aluminium anodized at 22 V in 0.1 M H$_2$SO$_4$ at 0 °C (figures a and c) and 20 °C (figures b and d); A and F – control specimen; B and I - 0.1% fluorozirconic acid; K and O - 0.5% fluorozirconic acid; C and H - 0.1% fluorosilicic acid; L and P - 0.5% fluorosilicic acid; D and J - 0.1% fluorotitanic acid; M and Q - 0.5% fluorotitanic acid; E and G - 0.1% fluoroboric acid and N and R - 0.5% fluoroboric acid........................................................................................................................................147

Figure 7-2 Current-density-time curves for AA 2024-T3 alloy anodized at 22 V in 0.1 M H$_2$SO$_4$ at 0 °C (figures a and c) and 20 °C (figures b and d); A and F – control specimen;
B and I - 0.1% fluorozirconic acid; K and O - 0.5% fluorozirconic acid; C and H - 0.1% fluorosilicic acid; L and P - 0.5% fluorosilicic acid; D and J - 0.1% fluorotitanic acid; M and Q - 0.5% fluorotitanic acid; E and G - 0.1% fluoroboric acid and N and R - 0.5% fluoroboric acid.

Figure 7-3. Scanning electron micrographs (backscattered electrons) of the surfaces of anodic films formed on aluminium in 0.1 M H$_2$SO$_4$ at 0 °C (top row) and 20 °C (bottom row). A and E – control specimens anodized without fluoroacid; B and G – 0.1 wt.% fluorozirconic acid (FZ); C and H – 0.1 wt.% fluorosilicic acid (FS); D and J – 0.1 wt.% fluoroboric acid (FB); E and K – 0.1% fluorotitanic acid (FT).

Figure 7-4. Scanning electron micrographs (backscattered electrons) of the surfaces of anodic films formed on AA 2024-T3 alloy in 0.1 M H$_2$SO$_4$ at 0 °C (top row) and 20 °C (bottom row). A and E – control specimens anodized without fluoroacid; B and G – 0.1 wt.% fluorozirconic acid (FZ); C and H – 0.1 wt.% fluorosilicic acid (FS); D and J – 0.1 wt.% fluoroboric acid (FB); E and K – 0.1% fluorotitanic acid (FT).

Figure 7-5 Scanning electron micrographs (secondary electrons) of the cross-sections of anodic films formed on aluminium in 0.1 M H$_2$SO$_4$ at 0 °C (top row) and 20 °C (bottom row A and E – control specimens anodized without fluoroacid; B and G – 0.1 wt.% fluorozirconic acid (FZ); C and H – 0.1 wt.% fluorosilicic acid (FS); D and J – 0.1 wt.% fluoroboric acid (FB); E and K – 0.1% fluorotitanic acid (FT).

Figure 7-6 Scanning electron micrographs (secondary electrons) of the cross-sections of anodic films formed on AA 2024-T3 alloy in 0.1 M H$_2$SO$_4$ at 0 °C (top row) and 20 °C (bottom row A and E – control specimens anodized without fluoroacid; B and G – 0.1 wt.% fluorozirconic acid (FZ); C and H – 0.1 wt.% fluorosilicic acid (FS); D and J – 0.1 wt.% fluoroboric acid (FB); E and K – 0.1% fluorotitanic acid (FT).

Figure 7-7. GDOES elemental profiles of aluminium anodized at 22 V for 300 s, in 0.1 M H$_2$SO$_4$ at 0 °C containing (a) no fluoroacid, (b) 0.1% fluorozirconic acid, (c) 0.1 wt.% fluorosilicic acid, (d) 0.1 wt.% fluoroboric acid and (e) 0.1 wt.% fluorotitanic acid. The
aluminium, oxygen, boron and fluorine intensities were multiplied by factors of 5, 10, 10 and 1 respectively. ................................................................. 155

Figure 7-8. GDOES elemental profiles of aluminium anodized at 22 V for 300 s, in 0.1 M H₂SO₄ at 0 °C, (a) 0.1, 0.5 and 1.0% fluorozirconic acid, (b) 0.1, 0.5 and 1.0% fluorosilicic acid, (c) 0.1, 0.5 and 1.0% fluoroboric acid (d) 0.1, 0.5 and 1.0% fluorotitanic acid. The profiles in the respective figures show the signal intensities at the wavelengths selected for detection of zirconium, silicon, boron and titanium.......................... 156

Figure 7-9 Experimental and simulated (solid line) RBS spectra for aluminium anodized at 0 °C in 0.1 M H₂SO₄ containing 0.1 wt.% fluorotitanic acid. ......................................................... 157
Abbreviations

SEM – Scanning Electron Microscopy
TEM - Transmission Electron Microscopy
EDX - Energy Dispersive X-ray spectroscopy
RBS - Rutherford Backscattering Spectroscopy
NRA - Nuclear Reaction Analysis
GDOES - Glow Discharge Optical Emission Spectroscopy
FZ – Fluorozirconic acid
FB – Fluoroboric acid
FS – Fluorosilicic acid
FT – Fluorotitanic acid
TSA – 0.53 M Tartaric acid/0.4 M Sulphuric Acid
Abstract
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Doctor of Philosophy

Influences of fluorine species on the anodizing behaviour of aluminium and AA 2024-T3 alloy

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The present study investigates the effect of fluorine species during anodizing of aluminium and AA2024-T3 alloy in sulphuric acid and tartaric-sulphuric acid (TSA) electrolytes. The investigation comprises four main parts;

(i) Effects of fluoride on barrier film formation on aluminium.
(ii) Effects of fluoride and fluorozirconic acid (FZ) on porous film growth on aluminium in sulphuric acid.
(iii) Effects of FZ on porous film growth on aluminium and AA 2024-T3 alloy in sulphuric acid and TSA.
(iv) Effects on anodizing of other fluoroacids (fluoroboric (FB), fluorosilicic (FS) and fluorotitanic acid (FT)).

The anodic films were examined by analytical scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy, Rutherford backscattering spectroscopy, nuclear reaction analysis and glow discharge optical emission spectroscopy.

The behaviour of fluoride ions during the growth of barrier-type films on aluminium was investigated in ammonium pentaborate solution with added sodium fluoride. Additions of up to $3.5 \times 10^{-3}$ M sodium fluoride had a negligible influence on the film growth. In contrast, $3.5 \times 10^{-2}$ M sodium fluoride reduced the efficiency to 60% as fluoride ions promoted field-assisted ejection of $\text{Al}^{3+}$ ions from the film. Incorporated fluoride ions migrated inwards at a rate about twice that of $\text{O}^{2-}$ ions, forming a fluoride-rich layer at the film base.

The study of the influence of FZ on formation of porous anodic films in sulphuric acid and TSA employed a range of anodizing voltages, electrolyte temperatures and anodizing times. Fluoroacid increased the growth rate, with a reducing influence as the temperature increased. The films contained fluoride and sulphate ions, zirconium was not detected. The fluoride concentration decreased with increasing temperature, whereas the sulphate concentration was unaffected.

Anodizing aluminium and AA 2024-T3 alloy in other fluoroacids resulted in similar influences on the anodizing behaviour as FZ. The differences in growth rate, film composition and film morphology were comparatively small and did not show a systematic dependence on the type of fluoroacid employed. Boron, silicon and titanium were not detected in the films.
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This thesis dedicated to the memories of

my Father Mustafa A. Elaish (1937-2014)


My Lord forgive me and my parents as they have brought

me up (with love) from childhood.

لِإِنَّ رَجُلِ الْعَمِّ السَّمَّىَ الْأَكْرِمَيْنِ الَّذِيْنَ كَانَ يَتَرْقَبُانِ
هَذِهِ الْمِثْلَةُ بِفَاحِضِ الصِّبْرِ، أَهْدِ خَلَاصَةً
بِحَتَى وَعَصْيَةٌ جَهَدِي عَرَفَانَا بِمَا بِذَلَّةَ مِن
أَجْلِ اِقْتَظَامِ هَذِهِ الْحَمْرَةِ الطَّيِّبَةَ.

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The following papers were published by the author during his PhD study:


1 Introduction

Aluminium is a passive metal [1]. However, it is very reactive to the environment, which causes an oxide or hydroxide thin film to form on the aluminium substrate. The air formed film is generally 1-5 nm thick, which may provide relatively little protection to the aluminium against corrosion in an aggressive environment [2]. The anodic oxide film is of great significance to the production of many types of surface finish of the metal. It is the basis of what is probably the most corrosion resistant finish of all, namely, anodic oxidation in its various forms that can increase the film thickness to the micrometre scale.

2xxx series aluminium alloys are widely used in the aerospace industry due to their low density and high specific strength [3]. Alloying 2xxx series alloy with elements such as copper improves the mechanical properties but gives rise to micro galvanic couples that increase corrosion susceptibility [4]. In order to provide effective corrosion control, anodizing in chromic acid has been commonly used [1]; however, hexavalent chromium species are known to be toxic and hazardous [5]. Consequently, health and environmental concerns [6], together with legal restrictions, have motivated research into the development of alternative anodizing baths.

A range of investigations has sought an alternative to chromic acids for the aerospace industry, such as mixtures of boric/sulfuric acids [7-9], or tartaric/sulphuric acids (TSA) [10, 11].

Fluoride ions and fluorine-containing anions are commonly present in solutions used for pretreatment of aluminium alloys, for example in acid cleaning, acid etching and chemical brightening baths and also in conversion coating baths, such as chromate, trivalent chromium and fluoro-zirconate-fluorotitanate baths.

Effects of the presence of fluorine ions on the formation of the anodic film on aluminium and aluminium alloys are still unclear on many aspects, some studies have been made to investigate the effect of fluoroboric acid on the pores size and its population density related to the fluoroboric acid concentration and anodizing temperature [12]. More recent studies examined the influence of ammonium hexafluorosilicate [13] and ammonium fluoride [13,
additions to oxalic acid on the formation of porous anodic films on aluminium. The addition of fluoride ions to an electrolyte has also been investigated in relation to the formation of porous anodic films on aluminium in oxalic acid [15]. Fluoride ions are also often used in anodizing magnesium [16], titanium [17] and zirconium [18].

However, the information provided on the morphology and composition of the films on aluminium and aluminium alloy was very limited and the role of the fluoroacid in the growth rate of the film, its effect; on the anodizing efficiency, film dissolution rate, film stress, film growth mechanism, were not considered.

1.1 Aims of the project

The primary aims of study are to determine the effect of fluorine species, specifically free-fluoride ions and different fluoroacids (fluoroboric, fluorosilicic, fluorotitanic and fluorozirconic acid) on anodic film growth on aluminium and AA 2024-T3 aluminium alloy and to identify possible practical benefits to the anodizing process, such as increasing the film growth rate. The effects of the fluoroacids additions were examined for anodizing in sulphuric acid and TSA. Sulphuric acid is commonly used in industry for anodizing of aluminium alloys [19].

1.2 Objectives of the project

1. To determine the migration rate of fluoride ions relative to that of oxygen species in anodic alumina and the consequence of the presence of free-fluoride ions in the electrolyte on the efficiency of film growth. For this purpose, anodizing of high purity aluminium in ammonium pentaborate electrolyte with additions of free-fluoride ions is used to form barrier-type films, with the film compositions examined to identify the concentration and distribution of fluorine. The film morphology, composition and film growth rate, of the anodic films formed are examined by a range of analytical techniques, including SEM, TEM, EDX, RBS, NRA and GDOES.

2. To determine the effect of free-fluoride and fluorozirconic acid additions on porous film growth on high purity aluminium in sulphuric acid, with a particular interest in the
influences of the free-fluoride and fluoroacid on the film composition, rate of film growth, and film dissolution.

3. To extend the study of the effects of free-fluoride and fluorozirconic acid to porous film growth on high purity aluminium in sulphuric acid to the commercial AA 2024-T3 alloy, in order to identify differences in the anodizing behaviour compared with high purity aluminium, and to include anodizing of the alloy in TSA, which is of current interest as a replacement for chromic acid anodizing.

4. To compare the effects of fluoroboric, fluorosilicic, fluorotitanic and fluorozirconic acids on porous film growth on high purity aluminium in order to identify whether significant differences exist between the influences of the various fluoroacids.

The study provides new information about the anodic film growth rate, fluorine ion migration rate, film morphology and composition for aluminium and AA 2024-T3 alloy anodized in sulphuric acid and in sulphuric/tartaric acid that is not currently available in the literature.

1.3 The thesis structure

The thesis is divided into nine chapters. The 1\textsuperscript{st} and 2\textsuperscript{nd} chapters consist of a general introduction on anodizing of aluminium and aluminium alloys. The 3\textsuperscript{rd} chapter details the experimental methodology and testing instruments. The results are divided into four chapters (4 to 7); the 4\textsuperscript{th} chapter presents the findings about the effect of fluoride ions in the barrier layer; the 5\textsuperscript{th} chapter provides new insights into the effect of the addition of fluorozirconic acid on aluminium; the 6\textsuperscript{th} chapter presents results on the effect of fluorozirconic acid on anodizing of AA 2024-T3 alloy in sulphuric and tartaric-sulphuric acids, the 7\textsuperscript{th} chapter ties together the common themes and examines the effect of different types of bonded fluoride on the anodic film. The final section gives a brief review of the study findings and identifies areas for further research.

Each chapter includes an introduction, the discussion of the obtained results and conclusions. Published results are presented in chapters four, five and six. Unpublished results are presented in chapter seven.
2 Literature review

This chapter presents general information about the anodic films, and the specific information required to contextualize the experimental results is presented in the introduction of each chapter.

2.1 Anodic films

Anodic alumina films are formed by anodizing aluminium and its alloys [20]. The films have attracted important attention due to their practical applications, for example, as a dielectric for aluminium capacitors, as bonding layers for organic coatings and as a protective coating on aluminium substrates in their service environments [1]. The anodizing could be carried out by AC or DC power supply.

2.1.1 DC anodizing

The anodizing process consists of two steps, firstly surface pre-treatment by mechanical, chemical, electrochemical [21, 22]. Surface chemical treatment for aluminium alloys includes: coupling agents, etchants and conversion coatings. Most chemical treatments are combined with precursor degrease and desmut steps [23] then anodizing carried out for the pre-treated specimens by connecting the aluminium electrode to a positive terminal of a power supply and connecting of an appropriate cathode to the negative terminal of the power source with both electrodes immersed in a suitable electrolyte.

Anodizing may be carried out by applying a voltage or current through a D.C power supply to the anodizing cell, which contains the two electrodes immersed in the electrolyte. At the anode, negatively charged anions are attracted to the aluminium. Oxygen ions released from $\text{H}_2\text{O}$ in the electrolyte solution react with aluminium cations on the aluminium surface and forms $\text{Al}_2\text{O}_3$. Oxide growth can occur at three possible sites, either at the metal/oxide interface, oxide/solution interface or within the anodic film. The cathodic reaction occurs on the counter electrode where hydrogen gas is produced.
2.1.2 AC anodizing

AC current anodizing processes are also available for formation of porous anodic films on aluminium and aluminium alloys [24-26]. High-temperature AC anodizing is currently of interest for high-speed coil [1, 23]. Thin film AC anodizing in hot sulphuric acid using short anodizing times eliminates the need for degreasing or etching stages, as sufficient cleaning action is caused due to the hydrogen evolved from the surface during the cathodic action of the AC current. The process is usually operated at high temperature, 80 °C in a 15% sulphuric acid bath at current densities on the order of 10 mA cm⁻² (rms) [27, 28]. It produces a surface lacking in the characteristic scalloped features found in DC anodizing processes.

2.2 Types of anodic films

The oxide grows during anodizing by ionic migration across the alumina film, which occurs under a high electric field [29, 30]. The film morphology depends on the selection of the electrolyte and the film-forming conditions. Consequently, films grown at high-current efficiency in near-neutral electrolytes at ambient temperatures are of uniform thickness and free of porosity; such films are termed ‘barrier films’ Figure 2-1 (a). This type of film can be grown to a thickness of hundreds of nanometers [31-36], their thickness is proportional to the anodizing potential with a ratio of approximately 1.2 – 1.4 nm V⁻¹ [1, 37]. Porous films are grown at low-current efficiency and result from anodizing in acid electrolytes, or selected alkaline electrolytes [38]. These electrolytes provide solubility of the aluminium ions [39-43]. The films show a relatively regular porosity, Figure 2-1 (b). The pores are normal to the aluminium substrate, the film consists of outer pores layer and inner thin layer, relatively compact barrier layer of scalloped geometry [44]. Thus, the porous film itself can be divided into two regions, a thin compact barrier region and a thicker porous region [37, 45]. The barrier layer thickness and the diameter of the major pores are proportional to the applied voltage with a ratio of ~ 1 nm V⁻¹ [45, 46].
2.2.1 Barrier-type films

Barrier-type films are usually formed in appropriate electrolytes, where the alumina is relatively insoluble, such as tartrate and borate solutions of pH 5-7. The films, therefore, grow at high efficiency and the applied current is used to produce the oxide film, with negligible loss of ions from the film to the electrolyte. However, the presence of flaws at the surface will cause a small loss of efficiency [47].

Plumb and Lewis [48], utilized radioactive tracers ($^{35}$SO$_4^{2-}$) to investigate the barrier-type film. They concluded that the growth of a small part of the film happens by inward migration of O$^{2-}$ anions, but the bigger part forms by outward movement of Al$^{3+}$ cations. Amsel and Samuel [49] said that mobile species were cations.

Under a constant applied potential, film growth continues until the Al$^{3+}$ cations and O$^{2-}$ anions cannot migrate through the formed barrier alumina, due to thickening of the film and reduction of the electric field. When anodizing under constant current, the potential increases linearly with time from the commencement of anodizing until the dielectric breakdown occur at a
relatively high-voltage value [50]. The films are composed of amorphous or microcrystalline $\gamma$-$\text{Al}_2\text{O}_3$ or $\gamma'$-$\text{Al}_2\text{O}_3$, as detected by electron or X-ray diffraction [51-54], and usually contain incorporated species from the used electrolyte [25]. Brock and Wood [55] found that the bulk temperature of the electrolyte and the electrolyte concentration had a slight effect on the ratio between the barrier layer thickness and the forming voltage. The ratio decreased with an increase of electrolyte temperature and increased with increasing electrolyte concentration. Dunn [56] confirmed the finding in a subsequent study.

Under certain conditions, barrier films have been considered to transfer slowly into porous anodic films. Factors such as temperature, current density and the time of anodic film formation have been reported to influence the morphology of the resultant films. Franklin [52] and Keller, Hunter [37] and Stirland and Bicknell [51] suggested that pore-like morphologies may form due to preferential dissolution at the outer surface. Vijh [57] showed a very fine “granular” morphology in films formed in slightly alkaline borate solution at room temperature and a porous morphology at higher temperatures.

Infrared spectroscopy and transmission electron microscopy techniques have been utilized by Dorsey [58, 59] who showed that the film grown in 2 M boric acid pH 4.5 at 60 °C consists of a duplex layer. In films formed in borate electrolyte at pH 9.7, Leach and Neufeld [60] revealed that at ambient temperature, a typical barrier morphology was produced, which changes to porous morphology at a higher temperature. Takahashi and Nagayama [61], Hoar and Yahalom [62] and Choo and Devereux [63] examined films were grown in borate and tartrate electrolytes after long periods of anodizing at a constant potential. They reported similar porous morphologies in the resultant films.

2.2.1.1 Flaws and crystalline structures in anodic films

The generation of flaws in the barrier film is generally associated with local heterogeneity, either surface topographical (geometrical) or compositional, in the metal substrate. The presences of flaws and crystalline structures in the amorphous barrier layer have been confirmed by many researchers [64-66]. The flaws are favoured places of pitting and dielectric breakdown, which affect the performance of the anodic films for corrosion resistance and electronic applications. Vermilyea [67, 68] revealed that the flaws were responsible for the
electronic conduction through anodic films formed on Ta, Nb, W, Zr, and Al in all the thickness ranges that were studied. The flaws had diameters in the range of 2-200 nm and with a density in the range of $10^8$ to $10^{10}$ m$^{-2}$, depending on the surface pre-treatment of the original aluminium and the film thickness.

Richardson, Wood and Sutton [69] investigated flaws in barrier films and classified them into two types: residual flaws arising from regions of impurities' segregation on the metal substrate, and mechanical flaws generated from a structural defect. They showed that flaws with a density of $10^4$-$10^6$ cm$^{-2}$ and diameter in the range from 50 – 200 nm were present in anodic films formed on 99.94 % aluminium, and flaws with a density of $10^8$-$10^{10}$ cm$^{-2}$ and 10-20 nm diameter were present in anodic films formed on an Al-Cu alloy.

Janik-Czachor et al [70] described the presence of flaws with different sizes, shapes and densities; they proposed that pits were initiated at the base of these flaws and related the formation of the pits to salt accumulation and pH reduction.

Investigations by Thompson et al. [71-73] showed the location and precise morphology of flaws present locally in an amorphous barrier film; their formation mechanisms near surface impurity segregates were examined directly. It was suggested that current concentrates in the regions of impurities and segregates, and the localized temperature rise associated with Joule heating effects gives rise to the localized development of flaws comprised of crystalline alumina. The existence of regions containing $\gamma'$-alumina surrounding flaws in the films was confirmed by using transmission electron microscopy. These crystalline regions were more likely to appear when the anodizing potential was close to 100 V and their diameter increased rapidly with a further increase in the anodizing potential. It was noted that their population densities and their diameters were affected by an increase of the electrolyte temperature, but the electrolyte concentration and the applied current density had no significant effect. The metal surface condition has a strong effect on the population density of the crystalline regions, as their population density reduced from $2.4\times10^8$ cm$^{-2}$ on as received specimens to $10^5$ cm$^{-2}$ on electropolished specimens.

Shimizu and Tajima [74] showed that the population density of flaws was decreased by cleaning and electropolishing of the aluminium specimens before anodizing in ammonium
borate, as the estimated population density of flaws decreased from $2 \times 10^8$ cm$^{-2}$ on as-received specimens to $3 \times 10^7$ cm$^{-2}$ on chemically cleaned specimens and to $10^5$ cm$^{-2}$ on electropolished specimens.

Stirland and Bicknell [51] studied the effect of the anodizing voltage on the structure of nonporous alumina anodic films formed in 3% boric acid mixed with 0.05% borax, using electron microscopy and electron diffraction methods. They revealed that amorphous anodic films were more likely to form at low anodizing voltages of less than 100 V. Some $\gamma'$-alumina was present, mainly in the amorphous anodic film formed at higher voltages, and the amount of crystalline oxide increased with increasing anodizing voltage.

Crossland et al [75], in a study of the anodic film formed by anodizing of aluminium-2.5 at. % Mn alloy in 0.01 M ammonium pentaborate at a constant current density of 50 A m$^{-2}$ at 20 °C, concluded that one reason that flaws exist in anodic films is due to oxygen bubbles that are generated in the film as a result of oxidation of the alloying element.

Habazaki et al [76], in anodizing of an aluminium/chromium, sputtered alloy in 0.01 M ammonium pentaborate anodizing solution at a constant current density of 50 mA cm$^{-2}$, stated that the generation of oxygen led to the formation of gas-filled bubbles within the film and that the efficiency of the film growth decreased when the oxygen-filled bubbles collapsed and resulted in damage of the anodic film.

Zhou et al [77] from a study of anodizing of aluminium-1 atom % copper alloy in ammonium pentaborate electrolyte, concluded that the growth of the oxygen bubbles is assisted by ionic migration processes within the anodic film, which reveals a liquid-like a behaviour.

Zhuravlyova et al [78] concluded that the oxygen is produced in the anodic film as a result of oxidation of the anodic film material, which is catalyzed by the incorporation of non-valve metal species. Studies have shown that the generation of oxygen bubbles may be associated with the formation of a layer enriched in the alloying element, located immediately beneath the anodic film formed on Al-Cu [79] and Al-Cr [80] alloys. The subsequent incorporation of copper and chromium species results in the generation of bubbles of oxygen gas within the film due to the formation of regions of semiconducting oxide.
2.2.1.2 Anion incorporation in barrier layers

Barrier anodic films usually contain incorporated ions derived from the forming electrolyte anions or electrolyte-derived impurity species that significantly influence the chemical, physical and electronic properties of the films. Furthermore, the distributions of such species are determined by the relative migration rates of the incorporated species [35, 81-83]. For example phosphors, boron, chromium and a tungsten species may be incorporated into barrier films to certain depths from the suitable electrolyte.

Randall and Bernard [84], used radioactive tracer techniques to investigate anodic film formed in phosphoric acid electrolytes; the results showed the presence of a phosphate-free region in the inner third of the film thickness; this result agreed with that of Rabbo et al [85].

Konno et al [86] investigated films grown on aluminium in a phosphate solution, they found three layers were formed; the inner layer at a depth of 60-75 nm, contains Al$_2$O$_3$, and the intermediate layer at a depth of 20-50 nm, consists of AlO$_{1.463}$ : (PO$_4$)$_{0.025}$, and the outer part at a depth of 5-15 nm, comprises AlO$_{1.09}$ : (OH)$_{0.74}$ : (PO$_4$)$_{0.025}$. The film contained about 4.7 % of PO$_4^{3-}$. Abd Rabbo et al. [85], using secondary ion mass spectroscopy (SIMS), revealed AlO$^-$ and PO$_2^-$ secondary ion profiles for films formed in a neutral phosphate solution, which suggested that phosphorus, probably as phosphate, is incorporated within the outer two-thirds of the film. The inner one-third is apparently phosphate-free, within the limits of sensitivity of the technique. Thompson et al. [87] examined ultramicrotomed sections of barrier films formed in a neutral phosphate electrolyte directly using a combination of scanning transmission electron microscopy (STEM) and energy dispersive analysis of X-rays (EDAX) and confirmed the results of Rabbo et al. [85] Konno et al. [86] and Takahashi et al. [88] used a technique consisting of chemical dissolution (sectioning) of the oxide in a sulphuric acid, followed by impedance measurements, solution analysis and electron microscopy to determine the in-depth anion distribution in barrier alumina films formed in neutral phosphate solution. They found that both the phosphate concentration in the outer layer and the thickness ratio between the outer and inner layers, increase with current density applied but do not change with anodizing time or total film thickness at constant current density. Some results of their findings are also consistent with findings by using SIMS analysis. Takahashi et al. [38] later
found that with increasing pH of the phosphate solution, the thickness of the outer layer containing phosphate increases, and the phosphate concentration in the outer layer decreases; the thickness ratio of the outer layer to the whole oxide film increases until attaining a steady value of 0.8 above pH 6.5.

Rabbo, Richardson and Wood [85] measured the in-depth profile of chromium in films grown in neutral chromate solution. The surface of the film contains a chromium-rich layer with a thickness of a few nanometres; the level then drops rapidly to a low but detectable yield in the remaining film. Chung et al. [89] employed X-ray absorption spectra to study anodic alumina films formed in chromate solutions and suggested that the films contained chromium species in both Cr(III) and Cr(VI) states. It was suggested that chromate and dichromate species were adsorbed at the film/electrolyte interface and incorporated into the thickening film. A field-induced transformation probably occurs and generates outwardly mobile Cr$^{3+}$ ions. Shimizu et al. [90] using glow discharged optical emission spectroscopy (GDOES) depth profiling, investigated barrier films formed in sodium chromate solution. An extremely fine band, 2-3 nm thick, was present with a relatively high concentration of chromium species. The band separates an inner pure Al$_2$O$_3$ layer next to the metal, and an outer layer doped with low concentrations of CrO$_4^{2-}$ and Cr$_2$O$_3$.

The distribution of boron-containing species has been confirmed by Skeldon et al [91] using Rutherford backscattering spectroscopy (RBS) and by Shimizu et al. [34] by using TEM electron-beam, to induce crystallization structure section in the barrier films. It was claimed that the film consists of an inner region of pure alumina and an outer region of alumina contaminated with electrolyte anions. Later GDOES depth profiling analysis confirmed that the proportion of the outer boron-doped layer to the total film thickness is 0.44 [90, 92]. Shimizu et al. [93] examined ultramicrotomed sections of barrier films formed in a sodium tungstate solution; transmission electron micrograph showed directly a relatively dark region of film containing tungsten with a high electron scattering cross section. A combination of TEM and energy-dispersive analysis of X-rays (EDAX) and electron beam induced crystallization confirmed that the outer 30% of the total film thickness contains tungsten, with the underlying film being relatively pure alumina.
Shimizu, Thompson and Wood [34], utilizing ultramicrotomy allied with transmission electron microscopy, following anodizing in borate solution, found that the inner region of the barrier-type film contained very little borate anions. When this film section is exposed to an electron beam of the electron microscope, it changes easily to a crystalline material. However, the outer part containing anions does not change.

Bernard [94] agreed that both anions and cations are mobile, and that metal ion transport predominates. Konno, Kobayashi, Takahashi and Nagayama [95], using X-ray photoelectron spectroscopy (XPS) analysis of films grown in a neutral borate electrolyte, found that the composition of the inner part is AlO$_{1.5}$ (B$_2$O$_3$)$_{0.027}$, whereas the outer region contains AlO$_{1.35}$ (OH)$_{0.28}$ (BO$_3$)$_{0.07}$ and this part is slightly hydrated. The average quantity of borate in the films is 5.8 % wt. However, these results were changed by the same authors, the exterior part was later reported as AlO$_{1.29}$ (OH)$_{0.28}$ (BO$_2$) and the interior part as AlO$_{1.473}$ (BO$_2$)$_{0.054}$.

Investigations by Skeldon et al [35], used Rutherford backscattering spectroscopy (RBS) to determine species incorporation from the electrolyte and the mobility of incorporated ions under the electric field. Generally, the film growth by Al$^{3+}$ outward migration and OH$^-$ and/or O$^{2-}$ inward migration through the pre-existing air-formed film; electrolyte species incorporation proceeds at the film-solution interface. Interestingly, electrolyte species incorporated in the film may be mobile inwards, immobile or mobile outwards as a result of their transformation under the field. Anodizing was performed to produce ~ 100% efficiency growth of a barrier layer, used xenon markers to measure relative mobilities of species. The xenon marker was located at 0.4 of the total anodic film thickness measured from the film/electrolyte interface. The position of the electrolyte anions in the barrier layer or their transformation products with respect to the xenon marker is an indication of their behaviour.
Figure 2-2  Schematic illustrations of ultramicrotomed sections of various kinds of barrier-type films formed on aluminium. (a) The relatively uniform thickness and textureless on initial examination. (b) Location of a xenon marker, which is directly visible in TEM as fine bubbles in the film sections. The xenon is found at a depth of about 0.4 of the total barrier layer film thickness measured from the film surface. (c) Section of the barrier film created in aqueous borate solution and subsequently exposed to the electron beam to induce crystallization of the interior film region. The crystallized inner film region extends from the metal/film interface to the position of the xenon marker revealed in (b), which indicates that boron species are immobile. (d) Section of the film formed in phosphate solution and afterwards exposed to the electron beam to induce crystallization of the internal film region. The crystallized internal film region extends to 0.3 of the full film thickness from the metal/film interface and does not reach the marker layer; this indicates that incorporated phosphate species are mobile inwards. (e) Section of the film formed in molybdate solution, with the exterior molybdenum-containing layer revealed by an atomic number contrast effect. (f) Section of molybdate film exposed to the electron beam. Subsequent crystallization extends to the external region containing incorporated anions and indicates that the molybdenum species are mobile outwards [35].
Species incorporated from borate, arsenate and silicon electrolytes are immobile in the film, as they can be incorporated only in the outer film regions developed by migration of by Al\(^{3+}\) ions. While phosphate was present below the marker layer extending to 0.7 of the film thickness from the film/electrolyte interface, indicating that these species are mobile inwards. With molybdate and tungstate electrolytes, species are located near the film/electrolyte interface, indicating outward mobility. Figure 2-2 shows schematically the behaviour of the incorporated ions in the anodic film.

Negatively charged incorporated anion species would migrate inward, whereas others anions may transform within the film into a positively charged product which would then move outward. Immobility is due to the transformation products being held rigidly in the random network of the amorphous alumina, probably due to the strength of their bonding with oxygen compared with the bonding of aluminium with oxygen.

### 2.2.1.3 Barrier layer formation mechanism

The anodic oxide is formed on the aluminium surface due to ionic migration under a high-field strength of \(10^8 \text{ – } 10^9 \text{ V m}^{-1}\) [64]. The oxygen for the oxide formation is derived mainly from the water molecules adsorbed on the surface [96, 97]. It has been proposed that hydrogen bonds are formed between the adsorbed water molecules and the adsorbed divalent oxyanion from the electrolyte, thereby weakening the O-H bonds in water molecules [97]. This effect, combined with the electric field, which polarizes the bonds, leads to release of \(O^{2-}\) or \(OH^-\) ions [97]. Both cations and anions within the film are mobile under the electric field during film formation. During barrier-film formation, at high-current efficiency, Al\(^{3+}\) ion egress and \(O^{2-}\) /\(OH^-\) ingress proceeds across the pre-existing air-formed film to develop solid material at the film/electrolyte and metal/film interfaces respectively [98, 99]. This is shown schematically in Figure 2-3.
With barrier film growth, oxide formation occurs at the metal/film interface and oxide/electrolyte interface; for porous film formation, growth proceeds only at the metal/oxide interface [98, 99]. The principal equations for these reactions are as follows:

\[
2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \\
\text{or} \\
2\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}^+ \\
\text{or} \\
2\text{Al}^{3+} + 3\text{O}^{2-} \rightarrow \text{Al}_2\text{O}_3
\]

About 40% of the ionic current in the anodic film is due to aluminium cations; the remaining current is due to \(O^{2-}/OH^-\) anions [100]. If there is no loss of species from film to the electrolyte, then about 40% of the film thickness is developed at the film/electrolyte interface and 60% at metal/film interface, i.e. 100% efficiency. Figure 2-4 shows schematically the cation and anion migration in the anodic film.
Figure 2-4  Schematic diagram showing the formation of a barrier type anodic alumina film on high purity aluminium, at high efficiency [100].

The position of an immobile inert marker, such as a thin layer of xenon, ion-implanted into a very thin preformed anodic film, reveals that the film forms by inward migration of $O^{2-}$ ions and by outward migration of $Al^{3+}$ ions. The xenon does not show the significant spread in the anodic film [101].

The kinetics of the ion transfer in the oxide film was studied by Gunterschultze and Betz [102]. They derived an empirical relationship between the non-ohmic ionic current density, $i$, and the electric filed strength, $E$,

$$i = A \exp(BE)$$  \hspace{1cm} 2-4

Where $E = V/d$, ($V$ is the potential drop across the oxide and $d$ is film thickness), $A$ and $B$ are temperature dependent constants. The relation is characteristic of the high-field conduction, and this expression shows the relation between the current density and the voltage at a particular film thickness.
The dependence of the ionic current within the anodic film [97], on the electric field strength has been expressed as follows:

\[ i = i_o \exp\left(-\frac{W_e(E)}{RT}\right) \tag{2-5} \]

Where

- \( i \) = Ionic current
- \( i_o \) = pre-exponential constant dependent on the transport medium
- \( W_e(E) \) = effective activation energy for ionic migration
- \( E \) = electric field strength
- \( R \) = universal gas constant
- \( T \) = temperature

The effective activation energy is taken as a linear function of the electric field strength according to the following equation:

\[ W_e(E) = Q - \alpha E \tag{2-6} \]

Where

- \( Q \) = Activation potential barrier for ionic transport under zero electric field
- \( \alpha \) = Transport medium related constant.

Other workers [103], due to several factors, such as the effect of polarization under the high electrostatic field on the transport medium and the consequent charge displacement [103], the electrostriction pressure [104], the anions species incorporated into the film [105], and the distribution of transport medium properties [106], have modified the previous equation by introducing a quadratic term for the field as follows.

\[ W_e(E) = Q - \alpha E + \beta E^2 \tag{2-7} \]

Where

- \( \beta \) = constant dependent on the migration medium.
The magnitudes of the constants and activation barrier are contingent on the mechanism of ionic transport in the film. Many theories of ionic migration have been proposed. These theories are often based on ionic migration across a crystalline lattice by Frenkel defects [107, 108]. Many of these theories are not entirely applicable to aluminium oxide, due to its amorphous nature.

2.2.1.4 Anodic film hydration

Brock and Wood [55] they found that the anodic film growth mainly by migration of aluminium and oxygen in a non-aqueous solution; little or no hydration of the film occurs. In an aqueous solution, hydration is more likely to occur especially at lower current density. Anodizing under low current density in a tartrate solution of pH 7 forms an anodic film with a relatively high degree of hydration. They proposed that the following reactions occur at the film/ electrolyte interface during film formation.

\[
2\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ \\
2\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}^+
\]

The current density-pH response will control the hydration at the film surface. By reducing the current density OH\(^-\) ions in the solution increased, which cause the hydration and partial dissolution of the film. If the current density raised so H\(^+\) ions will be produced faster and therefore, lowering the hydration of the film.

Konno et al [109], by using X-ray photoelectron spectroscopy (XPS) to study the alumina barrier layer composition formed in neutral borate solution at a constant potential of 50 V, revealed that specimens immersed in distilled water for 72 h gain more OH\(^-\) content in the outer film by a factor of 3 compared with un immersed specimens. They explained the results by the penetration of water molecules or OH\(^-\) ions into the oxide lattice. Further, they reported that the hydration process could be reduced by adsorbing of CrO4\(^{2-}\) and PO4\(^{3-}\) anions at the film surface.
**2.2.2 Porous-type anodic oxide films**

Porous anodic alumina films have been of research interest for many years, since they are important for the protection of aluminium alloys against corrosion and wear and provide surfaces adequate for the implementation of paints and adhesives [1, 37, 45, 46]. The films have also attracted significant attention for use in nanotechnologies, due to their sub-micrometre, ordered pores [110-113].

The most significant advances in understanding the morphology and structure of porous films arose with the advent of the transmission electron microscope. Setoh and Miyata [114] first proposed that porous anodic films have a duplex structure consisting of an inner barrier layer beneath a thicker porous layer. This concept was later confirmed by Keller et al. [37] who proposed a morphological model where pores are star-shaped and situated at the centres of close-packed, approximately hexagonal cells, whose diameter is a function of electrolyte type and forming voltage.

Porous-type anodic films form in relatively aggressive electrolytes. Thompson, Furneaux and Wood, [40] revealed that sulphuric acid is a suitable electrolyte for the formation of regular porous-type films. Thompson, Furneaux, Goode and Wood [41], used phosphoric acid to produce porous-type films. Chromic acid anodizing has been studied by Thompson, Wood and Hutching [42]. They confirmed that porous-type films can be produced. Oxalic acid, which is a convenient electrolyte to form porous films, has been used by Bailey and Wood [115]. They concluded that the acid electrolytes give relatively uniform porous-type films growth over the macroscopic metal surface under a variety of anodizing conditions.

Wood and O, Sullivan [46], investigated the effect of different anodizing factors on aluminium anodized in sulphate solutions. They revealed that raising the anodizing temperature produced thinning of the anodic film and increased the pore diameter, but with increasing the anodizing voltage the pore diameter and the film thickness increased. The increase in the current density led to an increase in the pore and cell diameters but a lower pore population density, while the thickness of the porous region increased with the charge passed during anodizing. The growth of the films involves the migration of Al\(^{3+}\) and O\(^{2-}\) ions in the barrier layer [96, 116]. Other species, derived from the electrolyte, may also be present in the films, such as phosphate or
sulphate ions, with differing migration rates, leading to compositional variation in the barrier layer and cell walls [101, 117, 118].

Hunter and Fowle [119] established a constant relation between barrier layer thickness and forming voltage during porous film formation. They found the ratios for anodic oxide films formed in 4 % phosphoric, 3 % chromic, 2 % oxalic and 15 % sulphuric acids were 1.19, 1.25, 1.18 and 1.0 nm V\(^{-1}\), respectively. Brock and Wood [55], reported that the ratio slightly depends on the concentration and the bulk temperature of the electrolyte. The ratio increases with increasing acid concentration and decreases with an increase of temperature of the electrolyte in agreement with the work in studies of Dunn [56]. Parkhutik and Shershulsky [120] found a linear relationship between pore size and the forming voltage for particular electrolyte conditions, and a dependency of pore size on solution pH where the pores become progressively larger as the pH is increased.

Paolini, Masaero, Sacchi and Paganalli [43] used an adsorption technique for measurement of pore volume. They defined the pore volume as the percentage or fractional volume of the film that consists of pores. They assumed that the pores are perfect smooth cylinders, and calculated pore diameters which were in conflict with results of Keller, Hunter and Robinson [37]. They calculated the porosities of anodic oxide films formed in sulphuric acid, chromic acid and oxalic acid electrolytes. The ratios of the true surface area to geometric area fell in the range 200-300:1.0 in a film grown in 15 % sulphuric acid to about 4 μm thickness. The range of the typical porosity was evaluated as 15- 25%. They thought that the volume of the pores is dependent on the thickness of the porous film, electrolyte temperature and concentration, and current density.

Porous film development is evident in voltage-time response curves for specimens anodized at constant current, and in current density-time response curves for specimens anodized at constant voltage [121]. These curves can be divided into four characteristic stages: in the first stage a compact barrier layer is formed, where the voltage (Figure 2-5(a)) increases and current density (Figure 2-5(b)) decreases in a quasi-linear manner up to a point corresponding to the maximum thickness of the barrier film. In the second stage, the voltage reaches a maximum, and the current density reaches a minimum. This stage corresponds to the initiation
of pores. The third stage starts at the top part of the voltage-time curve and at the bottom part of the current density-time curve and extends to the part where the curve rises again and reaches a constant value. These stages correspond to the widening and increase in the volume of the initial pores, which develop into their final morphology. The fourth stage starts when the current density reaches a constant value. In this stage, the thickness of the porous layer increases in thickness by sustained anodic oxide growth at the metal/oxide interface with increasing anodizing time, but the pore morphology (size and spacing) does not change.

Figure 2-5 Schematic diagram showing anodic film formation on high-purity aluminium, (a) Constant current anodizing, (b) Constant voltage anodizing [121].

The thickness of a porous anodic alumina depends on the charge passed during the anodizing. The charge increases with increasing the current density and anodizing time, while the current density depends on the anodizing parameters, such as electrolyte type, electrolyte concentration, anodizing voltage and temperature. However, the growth rate of the anodic alumina film formed on aluminium during ‘mild’ anodizing (constant voltage anodizing) has
been revealed to be in the range of 0.03 - 0.1 μm min\(^{-1}\) [122]. Hard anodizing processes produce a higher film growth rate of approximately 0.83 - 1.67 μm min\(^{-1}\) [123].

Since the work of O’Sullivan and Wood [45] on the detailed measurements of the early stages of pore initiation and growth, Thompson, Wood and others have revealed the sequences in the development of anodic film by examination of carbon replicas, stripped [41, 45] and ultramicrotomed [41] sections of anodic films in the transmission electron microscope. The stages are marked on the voltage-time and current density time transients. These porous regions of the film had a regular array of essentially parallel sided pores Figure 2-6 displays the nomenclature used for porous anodic film morphology.

![Figure 2-6 Schematic representation of a porous anodic film showing the principal morphological features [45].](image)

There is a non-uniform current distribution during initial film growth and pore development, with initial current concentration at the thickening regions, but eventually at the thin areas where the steady-state pores finally develop. As aluminium is consumed in the film growth, the metal/film interface becomes scalloped locally and spreads in a radial manner in order to maintain uniform field strength within this region. At this stage, the voltage is still rising in
order to maintain the constant field strength in this region with uninterrupted thickening of the barrier layer. The spread of the scalloped region causes the effective current density across the barrier layer to decrease in a similar manner. For this situation to proceed and to maintain a uniform field strength across the barrier layer, other pores competing for current must cease to grow [45].

When the scalloped regions merge at the metal/film interface, the hexagonal arrangement of the cell base pattern is created, more uniform local current density requirements are generated, and the film material thickens relatively uniformly, with the pore and cell diameters remaining constant. Thus, the steady-state growth of porous anodic film is developed.

2.2.2.1 Mechanism of porous initiation and growth

The growth of anodic films occurs at the metal/film interface due to inward migration of $O^{2-}$ ions across the barrier layer [96, 116]. Simultaneously, $Al^{3+}$ ions migrate outward and are ejected to the electrolyte solution at the pore base. Anodizing of aluminium has been successfully and widely applied for the synthesis of highly ordered nanostructures [111, 112, 124, 125]. It remains unclear as to which physical factors control pore ordering during oxide growth, and especially how the surface features of the aluminium affect the ordering of pores [126].

Porous alumina films characteristically consist of an inner barrier region and a much thicker, outer porous region. The latter contains fine, incipient pores on the film surface, which formed shortly after the start of anodizing, and larger, approximately cylindrical, major pores, which are present in the main body of the film. From a selected number of the incipient pores, the major pores are developed and incipient pore ceases to grow. It has been suggested that major pores form due to either dissolution of the oxide at the pore bases (dissolution model) [127] or flow of oxide [128-130] in the barrier region (flow model). Each major pore and the adjacent oxide constitute a cell, and under certain anodizing conditions, cells self-organize as a regular hexagonal pattern [131, 132].
2.2.2.1 Dissolution model

An early study conducted by Keller, Hunter and Rabinson [37], suggested that the pores start to initiate in the thinner sites of the oxide film. The local currents increased at these thinner points to increase the anodic film thickness and repair the damage that occurred due to the local dissolution of the oxide layer. This will lead to an increase in the electrolyte temperature at this point, and hence, more dissolution of the oxide takes place. These two factors control the sites of the pores and the subsequent processes that permit the porous film to increase in thickness. The pore and cell diameters were approximately twice the barrier layer thickness and proportional to the forming voltage. Formation of a porous anodic film type was proposed to occur as a result of the balance between the anodic film growth rate and the anodic film chemical dissolution rate by the electrolyte [37]. The pores formed similarly to the barrier layer, in which the pores were initiated at some areas arising from preferred attack by the electrolyte.

Hoar and Mott [127] suggested that major pores form due to the dissolution of the oxide and aluminium ions are ejected to the electrolyte at the pore bases as a result of a greater field strength at this point.

Hoar and Yahalom [62] suggested that the pores initiate as a result of oxide film dissolution due to the presence of hydrated aluminium oxides, which have lower specific electrical resistance than the anhydrous oxide, and lead to increase in the current density at favourable protonated spots. The electric field is concentrated on these points and subsequent local Joule heating in the adjacent electrolyte and in the film itself lead to further aluminium dissolution, such that a pore increases in depth.

Thompson et al [133] found that the thickness of the barrier layer remained constant, at a specific value under each pore, also the dimensions of the cell and porous approximately constant. The pore diameter, cell size and barrier layer thickness are directly proportional to anodizing voltage [45]. The equilibrium between film growth at metal/barrier film inner interface and field assisted dissolution at the outer surface of barrier film governed the film growth.
A finite-element method was adopted by Xu, [98, 134], to determine the potential distribution during the stages of initial film growth and development of penetration paths. For the initially developed film (Figure 2-7a), a relatively uniform potential distribution is evident in the film section. However, with the development of penetration paths through field-assisted dissolution (Figure 2-7 a, b, c), the potential lines remain relatively uniformly separated within the compact regions of the film but are concentrated immediately beneath the paths, indicating a local increase in field strength. The development of the penetration paths into the readily recognized pores arises and is assisted by the relatively strong lateral component of the field beneath the tip of the penetration path, resulting in its sidelong expansion to develop an embryo pore with its characteristic inversely funnelled sectional appearance.

![Figure 2-7](image)

Figure 2-7  Schematic illustrations of ultramicrotomed sections of anodic films corresponding to the introductory stages of pore development: (a) introductory growth of a relatively uniform alumina during the rising voltage region; (b) subsequent development of penetration paths into the alumina; (c) further development of penetration paths with a preferred development of the embryo pores and regions of disaggregated alumina at the film/electrolyte interface [98].

Xu, Thompson and Wood [135] suggested that the formation of a barrier or a porous film in a particular electrolyte is dependent upon the effective current density employed. The extent of solid-film formation at the film/electrolyte interface declines with a decrease in current density and electrolyte pH. For current densities below a critical value, film formation at the film/electrolyte interface is lost in local regions by field-assisted dissolution at preferred sites and a porous film is formed. The critical current density is dependent upon electrolyte type, concentration, pH and bulk electrolyte temperature. For electrolytes with relatively high chemical reactivity to alumina, the critical current density increases. The critical condition for
pore initiation in anodic alumina occurs when no film material forms at the film surface, i.e., all Al$^{3+}$ ions that migrate to the film surface are ejected into the electrolyte. This occurs at an efficiency of about 60% when the volume of formed oxide is approximately equal to the volume of metal consumed. Pore initiation was attributed to the instability of the film surface when subjected to the field-assisted dissolution of alumina at local regions where the field was enhanced. Pore-filling is prevented by the absence of growth of new oxide at the film surface, while increased stresses from electrostriction assist stabilization of the pores [98].

Overmeere et al [136], found that below 2 mA cm$^{-2}$ the aluminium dissolution is attributed to field-assisted dissolution of oxide while it was attributed to the direct ejection of aluminium to the electrolyte at higher current densities.

Nagayama and Tamura [137], according to their calculations, concluded that the rise of the temperature inside the pores base is always small and can be negligible. They used spectrophotometry on specimens anodized in 10 % H$_2$SO$_4$ for different intervals of anodizing time and concluded that the amount of aluminium dissolved during the first stages of the anodizing process is more than that dissolved during the formation of pores. Moreover, they calculated the rate of aluminium dissolution from the pore walls as 7.5x10$^{-9}$ cm min$^{-1}$ compared with 1.04 x10$^{-4}$ cm min$^{-1}$ from the bottom of the pores for anodizing at 11.9 V and 9.4 mA cm$^{-2}$.

Other workers, using O$^{18}$ as a tracer and nuclear microanalysis [96], reported that, as a result of high concentration of oxygen vacancies at the film/electrolyte interface, which originate from the adsorption of sulphate ions that retard the migration of oxygen ions, the formation of pores in anodic films on aluminium results from direct ejection of aluminium ions into the electrolyte after their high field migration to the pore base. Further, the pores do not form as a result of a simple oxide dissolution process, whether chemical or field-assisted. This process was referred to as field-assisted ejection of Al$^{3+}$ ions and was thought to be the most important step for the formation of porous aluminium oxide.

A recent study by Baron-Wiecheć and others [138], using arsenic as a tracer, on aluminium specimens re-anodized in phosphoric acid at a constant voltage of 110 V in a two-step anodizing procedure, showed that the incipient and major pores involve mainly field-assisted
dissolution and field-assisted flow of the anodic film respectively, as evident from the behaviour of an arsenic tracer.

2.2.2.1.2 Flow model

The flow model was developed to accommodate recent experimental evidence related to the increased film thickness with respect to the thickness of oxidized aluminium [139], by a factor of about 1.35 [140], incorporation of anions species into the film, oxygen tracer studies of porous films and the absence of tracer loss, with initially incorporated tracer being displaced to the cell walls [96], the displacement of heavy-metal markers during film growth [128, 129, 140-142]. and self-organization of pores is also envisaged through the redistribution of stress that follows attainment of a symmetrical pattern of pores [131].

Zhou et al [143, 144], in their study of anodizing of aluminium in sulphuric acid and oxalic acid, suggested that pores are initiated by dissolution at current densities below 2 mA cm\(^{-2}\) and by the flow of the anodic film at higher current densities. The transition may be due to the increase in the film growth efficiency and the amount of incorporated sulphur in the film, which increases with increase in the current density.

Skeldon et al [129] investigated the development of porosity in anodic alumina formed in 0.4 M phosphoric acid electrolyte by employing a tungsten tracer incorporated into a sputtering-deposited aluminium layer on a pre-anodized aluminium substrate, Figure 2-8 (b). The tungsten tracer was oxidized and incorporated into the barrier layer for specimens anodized in ammonium pentaborate, Figure 2-8 (c), retaining a flat morphology due to uniform outward migration of tungsten ions. In contrast, for specimens anodized in phosphoric acid, as shown in Figure 2-8 (d), associated with a scalloped metal/oxide interface, the tracer at was distorted, with tungsten in the barrier layer lagging behind that found at the cell walls Figure 2-8 (e and f). The behaviour is contrary to expectations of a field-assisted dissolution model of pore development, with usual migration behaviour of film species in the barrier layer. However, the findings are consistent with pore formation due mainly to flow of alumina from the barrier layer toward the cell walls, driven by film growth stresses. The flow of film material can also account for the increased thickness of the film relative to that of the oxidized metal.
Figure 2-8. Schematic diagram is showing the distribution of a tungsten tracer in anodic films. (a) Pre-anodized aluminium substrate with a barrier layer. (b) Sputtering-deposited aluminium with a tungsten tracer, (c) the tracer layer following incorporation into a barrier film. (d) The distorted tracer layer following incorporation into the barrier layer region of a porous anodic film. The distortion arises from the flow of alumina material from the barrier layer at the base of the porous toward the cell walls. The material flow proceeds as the anodizing time increase as shown in (e) and (f) [129].

Garcia-Vergara et al [141], in other experiments employing a tungsten tracer layer, proposed that oxide flow also occurred during anodizing of aluminium in 0.4 M sulphuric acid, [128]
0.4 M oxalic acid and 0.3 M malonic acid [142] electrolytes, at a constant current density of 5 mA cm$^{-2}$, with pores developing as a result of the flow of material from the barrier layer region beneath the pore bases towards the cell walls. The flow is accommodated by the increase in thickness of the anodic film by a factor of 1.35 relative to that of the thickness of the oxidized metal.

In other work [145], they compared the mechanism of pore development in 0.4 M sulphuric acid Figure 2-9 (a) with 0.13 M borax Figure 2-9 (b) at a constant current density of 5 mA cm$^{-2}$. They found that pores develop by the field-induced plasticity of the film for the film growth in sulphuric acid, and by field-assisted dissolution of the film grown in borax. Using 0.25 M chromic acid to anodize aluminium at a constant current density of 3 mA cm$^{-2}$ and at 40 °C, and investigating the film by TEM and RBS [146], the thickness of aluminium oxidized during anodizing was found to be equal to the anodic film thickness and the efficiency of anodizing was ~ 45-48%. Further, a tungsten tracer was lost to the chromic acid indicating that the major pores are formed mainly by field-assisted dissolution of the anodic film.

Oh, and Thompson [147] suggested that the incipient pores are developed by field-assisted dissolution at the anodic film/electrolyte interface. They reported that the electric field at the base of the pores is self-stabilized and increases with increase in the dissolution rate of the oxide at the pore base. Its increased the electrical field strength leads to further transfer of oxygen ions to the metal/oxide interface, which is necessary for the anodic film growth. They proposed that the pore growth is associated with plastic deformation and flow of the anodic film when the applied electric field reaches close to the final steady-state value.

Anodizing produced significant stress both in the oxide and at the metal-oxide interface. For oxides grown to 20 nm thickness, the oxide stress was tensile below 3 mA cm$^{-2}$ and compressive above this current density, while the interface stress exhibited the opposite dependence. Stress generation correlated with interfacial volume change due to reactions and transport processes: oxide or interface stress was compressive when the interfacial volume was created, and vice versa [148]. Compressive stress build-up in the oxide is apparently required for self-ordered pore formation by flow-assisted mechanisms. From this result, a simple criterion was derived specifying the conditions for compressive stress and pore formation in
terms of parameters governing film composition, ionic transport and interfacial reaction kinetics.

Figure 2.9. Schematic diagram illustrating qualitatively the differing behaviour of tungsten species incorporated into porous anodic films formed in (a) sulphuric acid and (b) borax. The diagrams show the progress of the tungsten species (dark band) through the barrier layer beneath a pore with an increase of anodizing time. (a) Showing field-assisted flow of oxide (flow model). (b) Showing field-assisted dissolution (dissolution model) [145].
2.2.2.2 Anion incorporation in porous layers

A porous anodic alumina film can contain several types of anion species. The species amount and the depth of incorporation in the anodic film depend on the electrolyte composition, its concentration and the anodizing parameters.

Thompson et al [149], using direct transmission electron microscopy of an ion-beam-thinned steady state porous anodic film, formed in phosphoric acid or oxalic acid, revealed that the distribution of the acid incorporated species is not uniform throughout the anodic film. The pore cell boundaries are free of phosphorus and contain only pure alumina, whereas phosphorus is detected in a greater amount in the film the next to the pores. For an anodic film formed in chromic acid, the analysis showed that there is no significant chromium in the pore cell material, which consists of relatively pure alumina. Additionally, for a film formed in sulphuric acid, the analysis showed that there is also a region of relatively pure alumina. Thompson and Wood [47, 149] based on the above information suggested that the ratio of the thickness of relatively pure alumina regions to the acid incorporated anions regions decreased in the following order:

Sulphuric acid (0.05) < Oxalic acid (0.1) < Phosphoric acid (0.5) < Chromic acid (∞).

Figure 2-10 shows the distribution of incorporated ions in the cell wall associated with each acid. It was expected from this finding that the rate of formation of the anodic films in the different acids at constant voltage increases in the same order as above. This is due to the difference in the thickness of pure alumina and the distribution of the incorporated acid anions.

The pore cell consists of an internal region which consists of a compact pure alumina region of differing thickness according to the forming acid and an external region, which contains the incorporated anions which may vary from solid material at the cell boundary bands to gel-like material at the base of the pores. The passage of the ions through the external region may then occur more easily than the internal region; the voltage drops quickly and linearly across the inner compact pure aluminium regions and decreases gradually in the outer layer. The thickness of these two layers controls how fast the voltage drop. So the incorporated species
from each acid and the true field strength across the relatively pure alumina can determine the anodizing behaviour of the porous anodic films formed by each acid. Figure 2-11 shows the distribution of voltage drop across the barrier layers of anodic films formed in different anodizing acids. The figure shows that the voltage drop is greatest and linear across the layer of relatively pure aluminium and lower in the outer region containing incorporated acid species, where the voltage decrease gradually towards the film-solution interface. As the result of this, the highest field is across the lower thickness of the relatively pure alumina which forms using sulphuric acid. The lowest field occurs for the thickest pure alumina layer in the film formed using chromic acid [47, 149].
Figure 2-10 Schematic diagrams showing the plan and cross section for the major anodizing acids: (a) sulphuric; (b) oxalic; (c) phosphoric; (d) chromic acid. The cell comprises acid anion contaminated film material next to the pore and relatively pure alumina where cells meet [149].
Figure 2-11  Distribution of the voltage drop and field (the slope of the voltage-distance plot) across typical barrier layers of porous anodic films formed in each of the major acids: a) sulphuric acid, b) oxalic acid, c) phosphoric acid, d) chromic acid [149].

2.3 Aluminium alloy

Aluminium is the most-used metal in the aircraft industry due to its low density 2.7 g cm\(^{-3}\), the relatively high corrosion resistance of the pure metal and a high mechanical strength that can be achieved by suitable alloying and heat treatments. However, the main alloying elements to improve the alloy strength are heavy metals, which decrease the corrosion resistance. High mechanical strength and high corrosion resistance are aircraft industry necessities. Therefore, the development of a range of protective high-strength alloys is important for the industry.

Aluminium alloys are classified according to their production process, chemical composition and heat treatment.
Alloying elements include; copper, manganese, silicon, magnesium, lithium and zinc. These alloying elements significantly influence the properties of aluminium alloys [150]. Magnesium reduces the melting point; it increases work-hardening ability and corrosion resistance to salted water. Copper gives great strength increase and allows cold precipitation hardening, but reduces corrosion resistance, weldability and ductility. Manganese increases strength either in solid solution or as a finely precipitated intermetallic phase. It has no adverse effect on corrosion resistance. Silicon increases strength and ductility and reduces the melting point. If combined with magnesium it allows precipitation hardening. Zinc drastically increases strength and allows hot or cold precipitation hardening. Other alloying components that are less significant from a corrosion-resistance standpoint are frequently included to improve mechanical and other physical properties. These are iron, chromium, titanium, zirconium, lithium and nickel [151].

Heat-treatable alloys can be hardened by controlling the heating and cooling cycle, were alloying elements dissolve into solid solution and precipitate as coherent submicroscopic particles. The heat-treatable alloys include the 2xxx, 6xxx and 7xxx series. The heat treating cycle include heating up to 450-530 °C, quenching with water or air, and ageing at room temperature (natural ageing) or heating the alloy to a temperature varying between 120 and 180 °C (artificial ageing) [152-154].

Non-heat treatable alloys, also called work-hardenable alloys, include alloys from the 3xxx and 5xxx series. The strength is increased by dispersion of second phase constituents or elements in solid solution and cold work the alloy [152].

AA 2024-T3 alloy. T3 applies to the alloys that are cold-worked specifically to improve strength after solution heat treatment and for which mechanical properties have been stabilized by room temperature ageing. This designation also applies to products in which the effects of cold work, imparted by flattening or straightening, are accounted for in the specified property limits[152].

Habazaki et al [79] studied the effect of Cu content on the pre-treated aluminium alloy. They found that anodizing of a mechanically polished Al-0.9 at % Cu alloy results in an initial film composed of relatively pure alumina. Simultaneously, copper is progressively enriched in a 2
nm thick layer of the alloy up to a concentration of 40 at% Cu. Once the copper enrichment has been established, the copper starts to oxidize and is incorporated into the anodic film and migrates outward faster than Al\(^{3+}\) ions. The incorporation of the copper ions generates flaws that reduce the uniformity of the anodic film. Chemical etching results also in an enrichment of copper similar to anodizing [155].

Habazaki et al [156] examined the effect of alloying elements on anodizing of aluminium alloy. They found the enrichment of alloy layers of about 1-5 nm thickness is revealed to be a common occurrence following anodizing of aluminium alloy. The enrichment is present in the alloy just beneath the anodic film, is a direct consequence of the formation of the anodic film on the alloy. Other surface treatments could generate the enrichment layer in the aluminium alloy, includes chemical polishing, electropolishing and alkaline etching.

Accumulation of the pressure of oxygen generated following oxidation of copper, together with the stress generated at the metal/film interface, may lead to cracks in the anodic film formed during anodizing of Al-1.86% Cu alloys in sulphuric acid [157].

Garcia-Vergara et al [158] concluded that anodizing of a sputtered Al-Cu alloy in phosphoric or sulphuric acid leads to enrichment of copper beneath the anodic film. Once this layer has been created oxidation of copper can begin and copper ions enter into the anodic film. Oxygen is then generated subsequent to the copper oxidation; following incorporation of copper ions oxygen is generated and bubbles of high-pressure oxygen gas form within the film. The stress due to the gas can cause plastic deformation of the oxide [159, 160]. The bubbles also lead to a non-uniform distribution of the ionic current that results in a less-uniform film thickness.

Skeldon et al [161] anodized Al 1 at% Cu alloy in ammonium pentaborate to study the composition of the produced anodic film. They found higher oxygen content in the anodic film compared with that formed on pure aluminium, which was related to the oxidation of copper in the enriched layer and the existence of high-pressure oxygen bubbles with a pressure of about 150 MPa. Dimogerontakis et al [162] observed that oxygen evolution at about 1.1 V s\(^{-1}\) occurs during galvanostatic anodizing of AA 2024-T3 aluminium alloy at 0.1 mA cm\(^{-2}\) in borate electrolyte. This oxygen evolution is related to the oxidation of copper-containing intermetallic particles. With the increase of the anodizing potential in the range from 20 to 40
V, the copper ions are incorporated into the film and the flaw population density in the anodic film is increased and results in weakening of the electrical characteristics of the film and increase of the current leakage.

Aluminium alloys are present in the fuselage aircraft, the most corrosion resistant aluminium alloys (6xxx series) are in the bottom part of the aircraft because such areas are prone to accumulation of fluids and liquids. Alloys with higher mechanical properties (2xxx and 7xxx series) are used in the upper and middle part of the fuselage.

AA2024-T3 is a high-strength, lightweight, aluminium alloy [163, 164]. Its high strength-to-weight ratio has seen it, its predecessors, and related variants used extensively in aircraft manufacture for many years. However, the alloy generally has low corrosion resistance [165-169]. Thus, the alloys are often anodized to improve their corrosion resistance.

AA 2024-T3 alloy can be anodized in different electrolyte such as; chromic acid [170], sulphuric/boric acids [8, 171], sulphuric/oxalic acid [172], a mixture of sulfuric acid, boric acid and phosphoric acid [173], sulphuric acid [174] and in a mixture of sulphuric/tartaric acid (TSA). Morphology and dielectric behaviour of films formed in sulphuric acid and in sulphuric/tartaric acids mixture are closely similar [10, 175-177].

The anodizing process and the properties of the anodic films are apparently influenced by the alloying elements. The anodic film formed on AA 2024-T3 alloy had layered appearance, developed from embryo cells; the causes of the altered film morphology on the alloy must relate to the consequences of the enrichment of copper, the presence of copper species and oxygen in the film, and the release of oxygen to the electrolyte, or a combination of these factors, and their interactions with the pore formation mechanism [174].

Schneider et al [178] used scanning electron microscopy combined with energy dispersive X-ray spectrometry to characterize the microstructure of AA2024 T351. Mainly three types of intermetallic (θ phase, S phase and an Al–Fe–Si–Mn–Cu phase) were identified.

Saenz de Miera et al [179] investigated the effect of 2xxx and 7xxx alloys phases on the local and general anodizing behaviour of the alloys. Electrochemical tests, with scanning and transmission electron microscopy, were used in their investigation. Under potentiodynamic
conditions, the observed anodic current peaks were related to the anodic oxidation of specific second-phase particles. At 0 V, magnesium containing particles, including S-phase, were preferentially removed from the alloy surface; at 5–6 V (SCE), the copper and/or iron-containing particles, such as θ phase and Al₇Cu₃Fe particles were anodically oxidized.

### 2.4 Fluorine species in anodic films

Few studies in the literature have investigated the effect of fluoroacids on anodizing of aluminium and aluminium alloys. One study has been made of anodizing aluminium at a constant current density in fluoroboric acid solutions at temperatures ranging from 0 to 30 °C [12]. The work revealed that porous films were formed, with a pore size and population density that depended on the concentration and temperature of the fluoroboric acid solution and the time of anodizing. However, the information provided on the morphology and composition of the films was very limited and the role of the fluoroacid in the growth of the film was not considered. More recent studies examined the influence of ammonium hexafluorosilicate [13] and ammonium fluoride [13, 14], additions to oxalic acid on the formation of porous anodic films on aluminium.

The addition of fluoride ions to an electrolyte has also been investigated in relation to the formation of porous anodic films on aluminium in oxalic acid [15]. A large reduction in the anodizing voltage was achieved by the addition of fluoride ions to the electrolyte. It was proposed that the reduction in voltage is related to the incorporation of fluoride-containing species into the anodic film. Fluoride ions are also often used in anodizing magnesium [16], titanium [17] and zirconium [18].

The previous studies provide relatively little information regarding the effect of fluoride ions and fluoroacid species on the anodizing of aluminium and aluminium alloy. Thus, information is lacking on key aspects of the anodizing behaviour and film properties including: effect of fluorine species on the anodizing efficiency; film composition, and incorporation and distribution of fluoride ions and fluoroacid species; film dissolution rate; film morphology; film growth mechanism; effect of the electrolyte concentration and temperature on the film growth rate.
The present study addresses these areas of deficiency, providing new information that assists understanding the role of fluorine species in the formation of anodic films and the effects of anodizing conditions on the film growth rate. The study employs anodizing of high-purity aluminium in (i) ammonium pentaborate to determine the migration behaviour of fluoride ions in anodic alumina and (ii) sulphuric acid-based electrolytes with additions of free-fluoride ions and fluoroacids to investigate the growth of porous films. Furthermore, the effect of fluorine species was examined in porous film growth on the commercially important aerospace alloy AA 2024-T3, in order to identify differences in the anodizing behaviour compared with high-purity aluminium due to influences of the alloying elements. The film morphology, composition and film growth rate of the anodic films formed are examined by a range of analytical techniques, including SEM, TEM, EDX, RBS, NRA and GDOES.
3 Experimental work

This chapter describes the materials employed, the experimental procedures and the methods used for specimen preparation, anodizing and testing. The techniques used for examination of anodic film, include scanning electron microscopy (SEM), transmission electron microscopy (TEM) imaging and elemental mapping, energy dispersive X-ray (EDX) analysis, Rutherford backscattering spectroscopy (RBS), nuclear reaction analysis (NRA) and glow discharge optical emission spectroscopy (GDOES).

3.1 Substrate Material

99.94 wt. % aluminium and AA 2024-T3 alloy specimens were anodized to create anodic films on the substrate surface.

3.1.1 Aluminium

Specimens of size 3 cm x 2 cm, cut from 99.94 wt. % aluminium foil of 0.3 mm thickness, were used as the substrate of specimens for the growth of barrier or porous anodic films. The nominal impurity composition of the aluminium sheet is determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) were; Fe 20 ppm, Si 480 ppm, Cu 50 ppm, Mg 10 ppm, with other elements less than 40 ppm wt%. The specimens were degreased with acetone and dried in a cool air stream.

3.1.2 AA 2024-T3 alloy

Specimens of AA 2024 T3 alloy (chemical composition determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) in wt. %: Cu 4.2, Mg 1.4, Mn 0.42, Si 0.06, Fe 0.07, Zn 0.03, Cr 0.01, and Ti 0.01), of dimensions of 10 mm x 50 mm was cut from a sheet of a thickness of 1 mm.

3.2 Electrolyte preparation

A number of electrolyte compositions were used in the study. The major part of the study employed sulphuric acid and sulphuric/tartaric acids containing various additions of fluorine
species to investigate the effect of such species on porous film formation. Additionally, ammonium pentaborate electrolyte used for the fundamental study of the behaviour of fluoride incorporated into barrier films.

3.2.1 Sulphuric acid

Two sulphuric acid concentrations were used for anodizing the aluminium and AA 2024-T3 alloy, 0.1 and 1 M sulphuric acid were prepared by adding of 5.33 and 53.3 cm$^3$ of concentrated sulphuric acid (H$_2$SO$_4$ > 95 % purity from Fisher Scientific) to 1000 ml of deionized water, respectively.

3.2.2 Tartaric/sulphuric acid (TSA)

TSA prepared by adding 0.4 M (40 g/L) sulphuric acid and 0.53 M (80 g/L, L-(-)-tartaric acid > 99 % purity supplied by Alfa Aesar) to 1000 ml of deionized water.

3.2.3 Ammonium pentaborate

0.1 M ammonium pentaborate was prepared by adding 54.4 g of ammonium pentaborate to 1000 ml of deionized water.

3.2.4 Fluoroacid additions

46% Fluorozirconic (FZ) acid (H$_2$F$_6$Zr), 50% fluoroboric (FB) acid (HBF$_4$), 35% fluorosilicic (FS) acid (H$_2$F$_6$Si) and 52% fluorotitanic (FT) acid (H$_2$F$_6$Ti), were supplied by Almetron Ltd. The fluoroacids were used as additions to the control acids. The fluoroacids contain free fluoride ions as well as bonded fluoride species. The fluoroacids supplier carried out an analysis of the free fluoride content, as described below; the results were used as a guide to estimate the free fluoride in the anodizing solutions, as shown in Table 3-1.

A commonly used method of measuring the concentration of fluoride ions is by an ion selective electrode. A fluoride ion selective electrode is a type of ion-selective electrode sensitive to the concentration of the fluoride ion. A common example is the lanthanum fluoride electrode. In the lanthanum fluoride electrode, the sensing element is a crystal
membrane of lanthanum fluoride (LaF₃), doped with europium fluoride (EuF₂). The inner surface of the crystal is in contact with the inner reference solution, and the outer surface of the crystal is in contact with the solution containing the fluoride ion. A potential develops across the membrane that depends on the difference in the concentration of fluoride ion on each side of the membrane. Since the concentration of the internal solution is fixed, the potential developed across the membrane is related to the concentration of the fluoride ion in the electrolyte solution. This was thought to be impractical in this instance, because the extent of interference of bonded fluoride is hard to assess, and also the relationship between the potential and the fluoride concentration is logarithmic, making small differences difficult to quantify.

An alternative method was to use a cell developed originally by Imperial Chemical Industries (ICI), which incorporates a silicon electrode and a platinum electrode. The cell is filled with the solution to be assessed, and the current is measured when a potential difference is applied between the electrodes. Whereas an ion selective electrode would be used at a pH above 3, when H⁺ and F⁻ ions would be dissociated, this cell is used at a pH below 2, when H⁺ and F⁻ are associated as HF. The solution is normally acidified with phosphoric acid to achieve this. Measurement is taken after stabilization of the current flow. A standard time of 6 minutes is used at Almetron.

In the present instance, it was necessary to employ a technique which would differentiate between the contributions from free fluoride (although associated) and bonded fluoride (as BF₄⁻, SiF₆²⁻, TiF₆²⁻, or ZrF₆²⁻). Three methods were attempted. In the first method, boric acid was added to the acid to react with the free fluoride and produce fluoroborate ions. Fluoride was measured before and afterwards so that the difference could be related to the free fluoride concentration.

In the second method, potassium hydroxide was added to the acid to precipitate out the relative insoluble potassium salt of the bonded fluoride. The solubility of these are KBF₄ 3 g l⁻¹, K₂SiF₆ 1.8 g l⁻¹, and K₂TiF₆ 12.7 g l⁻¹, whilst KF is very soluble at 920 g l⁻¹. (No information could be found as to the solubility of K₂ZrF₆⁻.) The fluoride could be measured after the addition, and this should be mainly due to the free fluoride left in solution.
The third method was to add magnesium sulphate to each of the acids, to precipitate out the relatively insoluble magnesium fluoride (solubility 0.073 g l$^{-1}$), whilst leaving the bonded fluoride species in solution. The solubility of magnesium fluorosilicate is 308 g l$^{-1}$, and the solubility of magnesium fluoroborate is 470 g l$^{-1}$. No values could be found for the solubility of magnesium fluorotitanate or magnesium fluorozirconate, but it seemed a reasonable assumption that they would be relatively high compared to magnesium fluoride. Fluoride was measured before, and after the magnesium sulphate addition so that the difference could be related to the free fluoride concentration.

It was decided that the fluoride cell would, in principle, be better to differentiate between the fluoride concentrations, rather than the ion selective electrode, although the solubility data is for neutral solutions and would probably differ somewhat from a pH of less than 2.

Table 3-1 Amount of free and bonded fluoride, determined using a silicon/platinum electrode cell, (1$^{st}$ row) before precipitation, after precipitation of the free fluoride (2$^{nd}$ and 4$^{th}$ rows) and after precipitation of the attached fluoride (3$^{rd}$ row).

<table>
<thead>
<tr>
<th>Measurements (as F$^{-}$)</th>
<th>HBF$_4$</th>
<th>H$_2$SiF$_6$</th>
<th>H$_2$TiF$_6$</th>
<th>H$_2$ZrF$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids at 1% v/v, in mg l$^{-1}$ (1)</td>
<td>390</td>
<td>300</td>
<td>965</td>
<td>1075</td>
</tr>
<tr>
<td>Method 1 (H$_3$BO$_3$), in mg l$^{-1}$ (2)</td>
<td>275</td>
<td>220</td>
<td>730</td>
<td>1000</td>
</tr>
<tr>
<td>Method 2 (KOH), in mg l$^{-1}$ (3)</td>
<td>200</td>
<td>160</td>
<td>540</td>
<td>770</td>
</tr>
<tr>
<td>Method 3 (MgSO$_4$), in mg l$^{-1}$ (4)</td>
<td>265</td>
<td>310</td>
<td>750</td>
<td>960</td>
</tr>
</tbody>
</table>
Table 3-2 Amount of free fluoride in the fluoroacids, derived from the results presented in Table 3.1.

<table>
<thead>
<tr>
<th>Derived Results (as F⁻)</th>
<th>HBF₄</th>
<th>H₂SiF₆</th>
<th>H₂TiF₆</th>
<th>H₂ZrF₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method 1 (H₃BO₃), in g l⁻¹ = 1-2</td>
<td>11.5</td>
<td>8</td>
<td>23.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Method 2 (KOH), in g l⁻¹ = 3</td>
<td>20</td>
<td>16</td>
<td>54</td>
<td>77</td>
</tr>
<tr>
<td>Method 3 (MgSO₄), in g l⁻¹ = 1-4</td>
<td>12.5</td>
<td>None detected</td>
<td>21.5</td>
<td>11.5</td>
</tr>
</tbody>
</table>

As shown in Table 3-2 methods 1 and 3 are in reasonably good agreement. Therefore, it seems that these results are probably correct and that the assumption of magnesium fluorotitanate and magnesium fluorozirconate is relatively soluble is accurate.

Method 2 gives different results, compared to methods 1 and 3 for fluoroboric and fluorosilicic acids, but significantly higher for fluorotitanic and fluorozirconic acids. This is probably because potassium fluorotitanate and potassium fluorozirconate have a high enough solubility at low pH to stay in solution and interfere with the measurement.

The amounts of free fluoride that were determined to be present in the fluoroacids were as follows: 12 g l⁻¹ in 50% fluoroboric acid, between 0 and 5 g l⁻¹ in 35% fluorosilicic acid, 22 – 23 g l⁻¹ in 52% fluorotitanic acid and 8 - 10 g l⁻¹ in 46% concentrated fluorozirconic acid. The highest values within the ranges were used to estimate the free fluoride content in the 0.1 M sulphuric acid anodizing electrolyte. The calculations made to determine the amount of free fluoride for electrolytes containing 0.1, 0.5 and 1.0 % fluoroacids additions are detailed in Table 3-3. The values in each of the columns (numbered 1 to 19) of the table were derived from the following:

1. Fluoroacid chemical formula and concentration percentage.
2. The concentration of free fluorine in fluoroacids in g/l; these values were obtained from the previous paragraph.
3. The weight of 100 ml of each fluoroacid in g.
(4) The density of each fluoroacid in g/ml calculated by weighing 100 ml from each fluoroacids (from column No.2).

(5) The weight of each fluoroacid need to be added to the control acid in g; weighing of the control acid (~ 500 ml) multiplied by 0.1% wt. ((500 ml x 1 gr /100 ml) = 0.5 gr).

(6) The weight of 100 ml of the control electrolyte in g.

(7) The density of the control electrolyte in g/ml calculated from the weight of 100 ml of the control acid (from column No.5).

(8) The weight of the control electrolyte in g.

(9) The volume of the control electrolyte in L, calculated by dividing the weight of the control acid by the density of the control acid (by dividing column No. 8 by column No.7 and dividing by 1000).

(10) The weight of each fluoroacid added to the electrolyte in g.

(11) The volume of each fluoroacid added in ml; calculated by dividing the fluoroacid weight by the fluoroacids density (by dividing column. No.10 by column No. 4).

(12) The amount of free fluorine added to the electrolyte in g; calculated by multiply the volume of the fluoroacid added in ml by the concentration of the free fluorine in the fluoroacids added to the control electrolyte g/l and dividing by 1000 to change the values from ml to L (by multiplying column No. 11 by column No. 2 and dividing by 1000).

(13) The amount of free fluorine added to the control electrolyte in mol, calculated by dividing free fluorine added to the control electrolyte in, g by the molecular weight of fluorine 18.998 (by dividing the value in column No. 12 by 18.988).

(14) Mol of free fluorine per litre, calculated by dividing the free fluorine added to the control electrolyte in mol by volume of the control electrolyte in L (by dividing column No. 13 by column No. 9).
(15) The weight of 100% F.A added in g/L, calculated by multiplying the weight of fluoroacid added to the electrolyte in, g by the fluoroacid concentration (by multiplying column No. 10 by column No. 1).

(16) The molecular weight of the fluoroacid in g/mol.

(17) The No. of moles of each fluoroacid in 0.5 L, calculated by dividing the weight of 100% fluoroacids added in g/L by the molecular weight of the fluoroacid (by dividing column No. 15 by column No. 16).

(18) The molar concentration of fluoroacids (1 L), calculated by dividing No. of moles of fluoroacid (0.5 L) by the volume of the control electrolyte in L (by dividing column No. 17 by column No. 9).

(19) The ratio of MF.A/MF, calculated by dividing the molar concentration of fluoroacid (1 L) by No. of free mol of F in 1 L (dividing column No. 18 by column No. 14).

3.2.5 Sodium fluoride addition

To determine the role of free fluoride ions in the anodizing process, 0.00035, 0.0035, 0.035 and 0.35 M sodium fluoride were added to 0.1 M sulphuric acid and to 0.1 M ammonium pentaborate. These amounts of sodium fluoride contain a concentration of free fluoride similar to or greater than that found in the fluoroacids, as shown in Table 3-3.
Table 3-3. Free fluoride in the electrolyte solution of 0.1 M sulphuric acid mixed with fluoroacids.

<p>| | | | | | | | | | | | | | | |</p>
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</tr>
</thead>
<tbody>
<tr>
<td>(1) F.A and its conc.</td>
<td>(2) Free F in F.A g/l</td>
<td>(3) weight of 100 cc of each F.A in (g)</td>
<td>(4) density of F.A g/cc</td>
<td>(5) weight % of F.A added</td>
<td>(6) Weight of 100 cc of the control electrolyte (g)</td>
<td>(7) Density of the control electrolyte g/cc</td>
<td>(8) Volume of the control electrolyte in L</td>
<td>(9) Volume of F.A added to the electrolyte in (g)</td>
<td>(10) weight of F.A added to the control electrolyte in g</td>
<td>(11) Volume of F.A added in ml</td>
<td>(12) Free F added to the control electrolyte in mol</td>
<td>(13) Free F added to the electrolyte in (g)</td>
<td>(14) mol of F/L</td>
<td>(15) weight of 100% F.A added in g/L</td>
</tr>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td>HBF$_4$ (50%)</td>
<td>12</td>
<td>139.05</td>
<td>1.39</td>
<td>0.1%</td>
<td>101.1</td>
<td>1.01</td>
<td>490.40</td>
<td>0.49</td>
<td>0.49</td>
<td>0.35</td>
<td>0.0042</td>
<td>2.23E-04</td>
<td>4.59E-04</td>
<td>0.245</td>
</tr>
<tr>
<td>HBF$_4$ (50%)</td>
<td>12</td>
<td>139.05</td>
<td>1.39</td>
<td>0.5%</td>
<td>101.1</td>
<td>1.01</td>
<td>505.00</td>
<td>0.50</td>
<td>2.53</td>
<td>1.82</td>
<td>0.0218</td>
<td>1.15E-03</td>
<td>2.30E-03</td>
<td>1.263</td>
</tr>
<tr>
<td>HBF$_4$ (50%)</td>
<td>12</td>
<td>139.05</td>
<td>1.39</td>
<td>1.0%</td>
<td>101.1</td>
<td>1.01</td>
<td>505.00</td>
<td>0.50</td>
<td>5.06</td>
<td>3.64</td>
<td>0.0437</td>
<td>2.30E-03</td>
<td>4.60E-03</td>
<td>2.530</td>
</tr>
<tr>
<td>H$_2$SiF$_6$ (35%)</td>
<td>5</td>
<td>132.01</td>
<td>1.32</td>
<td>0.1%</td>
<td>100.9</td>
<td>1.01</td>
<td>497.56</td>
<td>0.49</td>
<td>0.50</td>
<td>0.376</td>
<td>0.0019</td>
<td>9.91E-05</td>
<td>2.01E-04</td>
<td>0.174</td>
</tr>
<tr>
<td>H$_2$SiF$_6$ (35%)</td>
<td>5</td>
<td>132.01</td>
<td>1.32</td>
<td>0.5%</td>
<td>100.9</td>
<td>1.01</td>
<td>544.60</td>
<td>0.54</td>
<td>2.72</td>
<td>2.063</td>
<td>0.0103</td>
<td>5.43E-04</td>
<td>1.01E-03</td>
<td>0.953</td>
</tr>
<tr>
<td>H$_2$TiF$_6$ (52%)</td>
<td>22</td>
<td>148.22</td>
<td>1.48</td>
<td>0.1%</td>
<td>100.8</td>
<td>1.01</td>
<td>485.85</td>
<td>0.48</td>
<td>0.49</td>
<td>0.33</td>
<td>0.0072</td>
<td>3.79E-04</td>
<td>7.86E-04</td>
<td>0.252</td>
</tr>
<tr>
<td>H$_2$ZrF$_6$ (46%)</td>
<td>10</td>
<td>153.71</td>
<td>1.54</td>
<td>0.1%</td>
<td>101.0</td>
<td>1.01</td>
<td>513.93</td>
<td>0.51</td>
<td>0.51</td>
<td>0.33</td>
<td>0.0033</td>
<td>1.76E-04</td>
<td>3.46E-04</td>
<td>0.236</td>
</tr>
<tr>
<td>H$_2$ZrF$_6$ (46%)</td>
<td>10</td>
<td>153.71</td>
<td>1.54</td>
<td>0.5%</td>
<td>101.0</td>
<td>1.01</td>
<td>505.00</td>
<td>0.50</td>
<td>2.53</td>
<td>1.64</td>
<td>0.0164</td>
<td>8.65E-04</td>
<td>1.73E-03</td>
<td>1.162</td>
</tr>
<tr>
<td>H$_2$ZrF$_6$ (46%)</td>
<td>10</td>
<td>153.71</td>
<td>1.54</td>
<td>1.0%</td>
<td>101.0</td>
<td>1.01</td>
<td>485.50</td>
<td>0.48</td>
<td>4.86</td>
<td>3.16</td>
<td>0.0316</td>
<td>1.66E-03</td>
<td>3.46E-03</td>
<td>2.233</td>
</tr>
</tbody>
</table>
3.3 Anodic film formation

Prior to anodizing, surface pre-treatment is carried out in order to remove surface oxide and contaminants and to produce a reproducible surface condition for the subsequent growth of the anodic film. The pre-treatment process selected is dependent upon the application. It commonly involves several stages, such as degreasing, de-oxidation, de-smutting and rinsing.

3.3.1 Surface Pre-treatment

Surface pre-treatment for aluminium alloys can usually be classified as mechanical, chemical and electrochemical [21, 22]. These pre-treatments provide surfaces that are free from contamination, which may exhibit macro- or micro- or nano-scale roughness. The surfaces may also display mechanically stability, hydrolytic stability and wettability by adhesives. Mechanical treatments include abrasion methods usually combined with degreasing [180]. Surface chemical treatment for aluminium alloys include: coupling agents, etchants and conversion coatings. Most chemical treatments are combined with precursor degrease and desmut steps [23]. Etching is used to remove gross organic and inorganic contamination using alkaline or acid solutions. Such material might include protecting or press oils; machining lubricants; and corrosion products. Most alkaline cleaning solutions are of a propriety nature. For aluminium, they mainly consist of mixtures of sodium hydroxide, sodium carbonate, trisodium phosphate, sodium pyrophosphate or sodium meta silicate with a pH range between 9 and 11.

In the present study, the aluminium and AA 2024-T3 alloy specimens were pre-treated by electropolishing and etching respectively.

3.3.1.1 Electropolishing

Aluminium specimens were electropolished at 20 V for 180 s in a mixture of 60% perchloric acid and ethanol, with a volume ratio of 20:80, at a temperature below 10 °C, as shown in Figure 3-1. After electropolishing, they were rinsed sequentially with ethanol and distilled water. They were then dried in cool air steam and masked with lacquer (Stopper 45 McDermid) to define a working area on one side of 2 cm², as shown in Figure 3-2,
3.3.1.2 Etching

Etching of AA 2024-T3 alloy specimens was carried out in 10 wt. % NaOH solution at 60 °C for 60 s. The specimens were then desmutted in 30 vol. % HNO₃ solution for 30 s, and rinsed in deionized water and finally dried in a cool air stream.
3.3.2 Anodizing process

The process consists of immersion of the aluminium or its alloy in the anodizing cell and applying either a constant current or a constant voltage.

3.3.2.1 Constant current anodizing

Anodizing was carried out at a constant current density of 5 mA cm\(^{-2}\) in a two-electrode glass cell. Ammonium pentaborate electrolyte was chosen as a reference electrolyte since in the absence of added fluoride ions it allows the growth of barrier-type anodic films at high efficiency [181]. The electrolyte also results in incorporation of boron species into the film [182], which provide a useful marker in the film, as described later. In order to examine the behaviour of fluoride ions in films, 0.1 M ammonium pentaborate solutions were prepared with additions of various concentrations of sodium fluoride (NaF). The temperature of the electrolyte was 20 °C. During anodizing, the electrolyte was stirred using a magnetic stirrer. The anodizing employed a Model 6911 DC power supply. The voltage during anodizing was recorded on a PC. Anodizing was terminated at selected voltages, as explained later. In some instances, the specimens were anodized in two stages in order to determine either the dissolution rate of the anodic film in the electrolyte or the migration rate of fluoride ions in the film.
### 3.3.2.2 Constant voltage anodizing

Anodizing was carried out potentiostatically at selected voltages, electrolyte temperatures, fluoroacid or sodium fluoride additions and anodizing times. A two-electrode cell was used for anodizing individual specimens, with a cylindrical aluminium sheet of area 200 cm² acting as the cathode. The electrolyte was stirred using a magnetic stirrer during the growth of the films. The applied voltage was provided by a GPR-100H05 (Good Will Instrument Co.) power supply. The current passed through the cell during anodizing was recorded on a PC with in-house developed Labview software. When anodizing was ended, the specimens were immediately removed from the electrolyte and rinsed with deionized water.

The anodizing procedure consisted of connecting the specimen to the positive terminal of a DC power supply and aluminium sheet was connected to the negative terminal. The temperature of the electrolyte was controlled using a Julabo FL601 chiller, as shown in Figure 3-3.

![Figure 3-3. Schematic diagram of the anodizing process.](image-url)
3.3.2.2.1 Specimens anodized in sulphuric acid

Aluminium and AA 2024-T3 alloy was anodized at 22 V for 300 s and 1200 s at 0 °C or 20 °C in 0.1 M sulphuric acid containing 0, 0.1, 0.5 or 1 wt.% of 50% fluoroboric (HBF₄), 35% fluorosilicic (H₂SiF₆) or 46% fluorozirconic (H₂ZrF₆). The molar concentrations of the fluoroacids and free-fluoride ions added to the electrolytes are given in Table 3-3. The free-fluoride will form HF in the sulphuric acid. Electrolytes were also prepared using 0.1 M sulphuric acid with additions of sodium fluoride (NaF – Fisher scientific 99.0+ %) at concentrations from 3.5 x 10⁻⁴ M to 3.5 x 10⁻¹ M that covered the concentrations of free-fluoride in the fluoroacid-containing electrolyte. As well as anodizing in electrolytes prepared with 0.1 M sulphuric acid, films were as well formed at 22 V in 1 M sulphuric acid at 0 or 20 °C with and without the addition of 0.1 wt.% fluorozirconic acid.

3.3.2.2.2 Specimens anodized in TSA

Following industrial practice and Airbus anodizing procedures, anodizing was carried out in a mixture of 0.4 M sulphuric acid (40 g l⁻¹) and 0.53 M tartaric acid (80 g l⁻¹) at 0, 20 and 37 °C stepping the potential from 0 to 14 V and from 0 to 18 V at a rate of 2.8 and 3.6 V min⁻¹ respectively, followed by holding at 14 or 18 V for 1200 s [170, 183-185], as shown in Figure 3-4.

Figure 3-4. Schematic diagram is shown step anodizing procedure [185].
3.4 Anodic film examination

3.4.1 Scanning electron microscopy

Scanning electron microscopy (SEM) uses a focused beam of high-energy electrons to produce a range of signals from a solid specimen’s surface. The electrons are generated by an electron gun and accelerated to a particular energy, up to 20 keV, before energy focused and striking the specimen. The detected signals are secondary electrons (SE), backscattered electrons (BSE) and X-rays (EDX), which are emitted from the specimen as shown in Figure 3-5. Imaging is obtained by detecting the number of emitted secondary electrons and backscattered electrons formed by scanning the electron-beam row by row over the specimen surface. X-rays are used to assess the composition and distribution of elements in the specimen.

![Diagram of SEM signals](image)

Figure 3-5. Origin and information depth of secondary electrons (SE), backscattered electrons (BSE), Auger electrons (AE) and X-ray quanta (X) in the diffusion cloud of electron range R for normal incidence of the primary electrons (PE) [186].

The atoms on the specimen surface interact with the electron beam and generate signals containing data regarding the specimen composition and surface topography. SEM gives higher magnification, larger depth of focus and finer resolution than optical microscopy. In the present work, anodic films were examined in cross-section and surface views using a Zeiss Ultra 55 FEG-SEM, as shown in Figure 3-6.
Observations of the surfaces and cross-sections of films were made by scanning electron microscopy (SEM) using a Zeiss Ultra 55 microscope operated at 1.5 keV. Cross-sections were prepared using a glass knife to trim the specimen to a proper thickness, followed by final cutting with a Micro-Star type SU diamond knife. The specimens were moved directly to the SEM chamber for observing the anodic film.

Compositional analysis of films was carried out using energy-dispersive X-ray (EDX) analysis (Oxford Instrument XMAX 80) in an FEI Quanta 250 scanning electron microscope with a silicon drift detector. For EDX analysis the microscope was usually operated at an accelerating voltage in the range 3 to 6 kV. The accelerating voltage was selected to avoid significant contributions to the X-ray yield from aluminium in the substrate. Selected specimens were also analysed using accelerating voltages of 10 and 15 kV. The detection limit of the EDX analysis was about 0.1 wt%. The accuracy of the resulting atomic ratios of F:Al and S:Al was estimated to be typically about ±15%.

### 3.4.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) of selected specimens was carried out using an FEI-Philips CM20 instrument, as shown in Figure 3-7 (a), operated at 200 kV. The electron gun generate the electron beam which accelerated by the condenser and objective.
aperture, then the transmitted beam through a suitably thin specimen focused by the projector lens.

An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, or to be detected by a sensor such as a CCD camera, as shown in Figure 3-7 (b). Sections of nominal thickness 20 nm were prepared using a Leica Ultracut microtome, with initial trimming of specimens using a glass knife and final sectioning using a Micro-Star type SU diamond knife.

TEM imaging and elemental mappings were carried out using a Titan G80-200 ChemiSTEM (FEI) instrument operating at 200 keV with four energy dispersive X-ray (EDX) spectroscopy detectors.

Figure 3-7, (a) Photograph of FEI-Philips CM20 and (b) schematic of the TEM column showing the main components [187].

3.4.3 Glow discharges optical emission spectrometer (GDOES)

Glow discharges optical emission spectroscopy (GDOES) is a technique which enables the evaluation of elemental concentration profiles of film materials. It is possible to obtain
information from the first few nanometers to the initial a couple of micrometres of the specimen depth. GDOES potentially has a high depth resolution and also high responsiveness for detection of elements. Consequently, GDOES with its ability of predictable and rapid analysis of films of thickness has an important role in studies on the corrosion and filming behaviour of materials [90].

Optical emission spectroscopy involves applying electrical energy in the form of a discharge created between an electrode and a metal specimen, whereby the vaporized atoms are brought to a high-energy state within a so-called "discharge plasma." These excited atoms and ions across the discharge plasma create a unique emission spectrum specific to each element.

The light generated by the discharge is a collection of spectral lines generated by the elements in the specimen. This light is split by a diffraction grating to extract the emissions for the target elements. The intensity of each emission spectrum depends on the concentration of the element in the specimen. Detectors measure the emission intensity of the spectrum to perform qualitative and quantitative analysis of the elements.

Elemental depth profiles of the anodized specimens were obtained using a Horiba Jobin-Yvon, RF-5000 glow discharge optical emission spectrometer (GDOES) at a frequency of 13.56 MHz and power of 50 W. Light emissions of characteristic wavelengths during sputtering using neon gas (1100 Pa) were monitored throughout the analysis with a sampling interval of 0.05 s. Use of neon gas was necessary to excite optical emission from fluorine. The wavelengths of the spectral lines used for the analyses were 396.152 nm (aluminium), 130.217 nm (oxygen), 685.602 nm (fluorine), 249.678 nm (boron) and 339.197 nm (zirconium).

In all GDOES figures, the element's profile magnified by multiply the oxygen intensity on 10, aluminium intensity on 5, boron intensity on 10 and the fluorine intensity on 1.

3.4.4 Chemical dissolution of porous alumina films

A re-anodizing technique was used to determine the dissolution rate of the barrier layer of porous anodic films formed on aluminium [188]. The barrier layer thickness after the chemical dissolution of anodic oxide films was determined using the resultant voltage/time curves. An aluminium specimen of size 12 x 80 mm was anodized at 22 V in 0.1 M sulphuric acid with addition of fluorozirconic acid for 1200 s and at 0 and 20 °C. The
specimens were rinsed in distilled water and then cut into several pieces. The pieces were immersed in the anodizing solution at the same temperature for selected times. The immersed specimens were then rinsed in deionized water and re-anodized at 5 mA cm\(^{-2}\) in 0.1 M ammonium pentaborate solution at 20°C using a constant current source Metromix model 6911. The voltage surge at the start of anodizing was measured. The thickness of the barrier layer was then calculated from the voltage surge using a ratio of 0.9 nm V\(^{-1}\).

### 3.4.5 Porosity measurement

Aluminium specimens were anodized in sulphuric acid at 22 V, with and without 0.1, 0.5 and 1.0 wt. % fluorozirconic acid, for 1200 s at 0 and 20°C. The anodized specimens were re-anodized in 0.1 M ammonium pentaborate at 5 mA cm\(^{-2}\) to 400 V.

The porosity of the films was determined from the ratio of the initial and final slopes of the voltage-time curves, the former being associated with the filling of the pores at their bases and the latter with uniform film growth where the pores were filled.

The porosity, \(P\), in the porous layer, is calculated by the following equation with transport numbers of \(\text{Al}^{3+} (T_{\text{Al}^{3+}})\) and \(\text{O}^{2-} (T_{\text{O}^{2-}})\) of 0.4 and 0.6 respectively [189, 190].

\[
P = \beta \frac{T_{\text{Al}^{3+}}}{1 - \beta T_{\text{O}^{2-}}} \tag{3-1}
\]

Where

\[
\beta = \frac{m_2}{m_1} \tag{3-2}
\]

\(m_2\) and \(m_1\) are the final and initial slopes of the \(v-t\) curve respectively.

### 3.4.6 Nuclear reaction analysis (NRA)

Nuclear reaction analysis (NRA) is a technique used to determine quantitatively the concentration of light elements in a film. NRA uses low mass ions such as protons or deuterons to induce a nuclear reaction with particular target atoms in the specimen. The emitted radiation from this reaction can be detected, as shown in Figure 3-8. From the emitted intensity, the concentration of the specific light element may be determined. Examples of reactions that are used for NRA include: \(^{16}\text{O} (d,p) ^{17}\text{O}\), \(^{19}\text{F} (d,p_{11, 12})^{20}\text{F}\), \(^{12}\text{C}\)
(d,p)\(^{13}\)C and \(^{14}\)N (d,p)\(^{15}\)N; for example, in the \(^{16}\)O (d,p)\(^{17}\)O reaction, a deuteron reacts with a \(^{16}\)O atom to form a \(^{17}\)O atom and emit a proton. The method is particularly useful for the determination of isotopic oxygen on or near the surface of solids, such as oxide films, silicates, etc. and for the isotopic investigation of very small quantities of organic materials. This technique of analysis is rapid and non-destructive [191].

In the present work, the oxygen contents of films were determined using a 1 mm diameter beam of 0.86 or 0.87 MeV \(^2\)H\(^+\) ions. Emitted protons were detected at an angle of 150\(^\circ\) to the direction of the incident beam. The reaction is given below by:

\[
^{16}\text{O} + d (^{2}\text{H}^{+}) \rightarrow ^{17}\text{O} + p (^{1}\text{H}^{+})
\]

A reference specimen of anodized tantalum was used to quantify the oxygen contents in the formed films.

3.4.7 Rutherford backscattering spectroscopy (RBS)

Rutherford backscattering spectroscopy (RBS) is a method used for a quantitative study of the composition of films. During an RBS measurement, elastic and inelastic collisions occur between the incident beam of the light ions (usually the He nuclei), at an energy in the range of 0.5-4 MeV, and the atoms of a target. The incident particles penetrating the target lose their energy because of interactions with the electrons and nuclei of the target, before being backscattered by nuclei of the target. The particle that is backscattered at a certain depth in the specimen will have less energy than that of the particle that is backscattered from an identical element located at the surface of the specimen. The energy distribution and the yield of the backscattered ions at a given angle are recorded. Thus, the RBS spectrum contains information on the nature of the various elements present in the target and their depth distribution.

The composition and growth efficiency of anodic films were determined by RBS, employing a beam of \(^4\)He\(^+\) ions at an energy of 2 MeV, produced by the Van de Graaff accelerator [192], at the University of Namur Belgium. The scattered ions were detected at an angle of 165\(^\circ\) to the direction of the incident beam, as shown in Figure 3-9. The analyzed specimen area was about 1 mm in diameter. Data were interpreted by using the RUMP simulation software.
Figure 3-8. (a) Schematic diagram of analysis of specimens using nuclear reaction analysis. (b) The principle of analysis of specimens using nuclear reaction analysis; the incident beam strikes the surface of the tested specimen and (c) an emitted particle from the nuclear reaction is detected with a given angle [193].
3.4.8 Nanoindentation hardness

The hardness of anodized specimens was measured using an MTS Nano Indenter XP instrument with a Berkovich diamond indenter. Thirty indentations were made for each specimen. The distance between the indentations was 100 µm, which was selected to maximize the tested area and to avoid the overlap between the indentations.

Figure 3-9. Schematic diagram of analysis of specimens using Rutherford backscattering spectrometry; the incident beam strikes the surface on the test specimen and is backscattered with a given angle [191].
4 Effects of fluoride ions on the growth of barrier-type films on aluminium

4.1 Introduction

Fluoride ions and fluorine-containing anions are commonly present in solutions used for pre-treatment of aluminium alloys, for example in acid cleaning, acid etching and chemical brightening baths [194, 195] and also in conversion coating baths, such as chromate [196-198], trivalent chromium [199-201] and fluorozirconate-fluorotitanate [202, 203] baths. During conversion coating treatments, fluoride ions have an important role in activating the alloy surface by thinning the pre-existing oxide film that is present on the alloy, thereby enabling the oxidation of the alloy and formation of the coating to proceed.

The addition of fluoride ions to an electrolyte has also been investigated in relation to the formation of porous anodic films on aluminium in oxalic acid [15]. A large reduction in the anodizing voltage was achieved by the addition of fluoride ions to the electrolyte. It was proposed that the reduction in voltage is related to the incorporation of fluoride-containing species into the anodic film. Fluoride ions are also often used in anodizing magnesium [16], titanium [17] and zirconium [18].

With regard to the behaviour of halide ions in anodic films formed on aluminium, studies of barrier-type films have revealed that chloride, bromide and iodide ions migrate inwards in amorphous anodic alumina during film growth [99, 204]. In these studies, the halide ions were incorporated into a thin anodic film by ion implantation. The films were subsequently increased in thickness by a further stage of anodizing. The movement of the ions was determined by locating the depth of the fluoride ions within the films using Rutherford backscattering spectroscopy. Since it was shown that the films grow by migration of Al$^{3+}$ ions outward and of O$^{2-}$ ions inward, with respective transport numbers of about 0.4 and 0.6 [99], it was possible to show that the chloride, bromide and iodide ions migrate inward more slowly than the O$^{2-}$ ions. In one study, the migration rates of chloride, bromide and iodide ions were determined to be about 0.58, 0.33 and 0.18 times that of the O$^{2-}$ ions [99]. In a second study, migration rates of about 0.72 and 0.29 that of O$^{2-}$ ions were derived for chloride and iodide ions respectively [204]. A further study incorporated chloride ions into a thin oxide formed during electropolishing in a perchloric acid solution and used secondary ion mass spectrometry to locate the chlorine in the
subsequently formed anodic film [205]. A relative migration rate of chloride ions of 0.62 was determined. The relatively small differences in the reported values of the migration rate of chloride ions from the various studies may be related to the different methods of chloride incorporation, ion doses and types of analysis. The relative rates of migration of chloride, bromide and iodide ions correlate with the differences in the ionic radii, with chloride having the smallest ionic radii (0.18 nm) and the fastest rate of migration and iodide ions having the largest ionic radii (0.22 nm) and the slowest rate of migration [99]. Hence, these ions are unable to migrate to the base of the film.

The migration rate of fluoride ions in anodic alumina appears not to have been measured. However, it has been shown that fluoride ions migrate inward faster than O$^2-$ ions during the formation of amorphous anodic films on tantalum [206] and titanium [207], which also grow by counter migration of cations and anions. The migration rates of the fluoride ions were about 1.85 and 2 times that of the O$^2-$ ions in anodic tantalum and anodic titania respectively [206, 207]. The relatively fast inward migration of fluoride ions is consistent with the smallest ionic radius among the halide ions (0.13 nm), although the ionic radius of fluoride ions is close to that of O$^2-$ ions (0.135 nm) [208], suggesting that ionic radius is not the only factor that influences the rate of migration.

The migration of ions within amorphous anodic alumina films appears to involve a cooperative process that links the movements of the various ionic constituents of the film in a single activation event. Hence, the kinetics of film growth can be explained by the high-field conduction mechanism [181]. Various atomic models have been proposed to explain the counter migration of the cations and anions [209-213]. However, none of these has been proven experimentally.

In view of the importance of fluoride ions for the surface treatment of aluminium alloys and the lack of a detailed study of the migration behaviour of fluoride ions in alumina films, the present work was carried out. It examines the effects of fluoride ions on the efficiency of growth and the composition of barrier-type anodic films on aluminium, including measurement of the migration rate of the fluoride ions in the films relative to O$^2-$ ions.
4.2 Results and Discussion

Figure 4-1 displays the dependence of voltage on time during anodizing of aluminium at 5 mA cm$^{-2}$ in 0.1 M ammonium pentaborate solutions containing additions of $3.5 \times 10^{-4}$ M, $3.5 \times 10^{-3}$ M, $3.5 \times 10^{-2}$ M and $3.5 \times 10^{-1}$ M sodium fluoride. The pH of the solutions was 7.6. The figure also shows the response to a fluoride-free solution. Anodizing in each solution was repeated three times with good agreement between the results. During the growth of the anodic film in the fluoride-free solution, the oxidized aluminium is retained in the film and side reactions are negligible [181]. The voltage displayed an approximately linear dependence on the anodizing time up to the onset of dielectric breakdown, with a gradient of about 2.3 V s$^{-1}$. Dielectric breakdown commenced at a voltage of about 325 V. Oscillations in the voltage then occurred and the voltage subsequently increased at a slower rate and eventually reached a limiting value of about 407 V.

Figure 4-1. Voltage-time curves for aluminium specimens anodized at 5 mA cm$^{-2}$ in 0.1 M ammonium pentaborate solution at 20 °C, with various additions of sodium fluoride. (a) A. No addition. B $3.5 \times 10^{-4}$ M NaF. C $3.5 \times 10^{-3}$ M NaF. D $3.5 \times 10^{-2}$ M NaF. (b) E $3.5 \times 10^{-1}$ M NaF.
4.2.1 The voltage-time curves

The voltage-time curves for the solutions containing $3.5 \times 10^{-4}$ M and $3.5 \times 10^{-3}$ M sodium fluoride were similar to that of the fluoride-free solution, indicating that the low concentrations of fluoride ions had little effect on either the film growth or dielectric breakdown. However, the addition of $3.5 \times 10^{-2}$ M sodium fluoride led to a significant reduction in the gradient of the response. The average value of the gradient in the period up to 200 V was about 1.4 V s$^{-1}$. The ratio of the gradient with respect to that under fluoride-free conditions, when film growth occurred at close to 100% efficiency [181], indicates that the film grew with an efficiency of about 60% due to loss of Al$^{3+}$ ions to the solution. The gradient of the curve gradually decreased with increasing the time of anodizing. Subsequent examination of a cross-section of the film formed to 200 V indicated that the film was tending to develop a porous structure. When the concentration of sodium fluoride was further increased to $3.5 \times 10^{-1}$ M, the voltage-time curve was the usual form for the growth of a porous film. Following a rapid rise in voltage to about 10.5 V, the voltage decreased to about 7.5 V then gradually increased to a final value close to 10 V.

![Figure 4-2 Voltage-time curves for an aluminium specimen anodized in two stages at 5 mA cm$^{-2}$ in 0.1 M ammonium pentaborate solution containing $3.5 \times 10^{-2}$ M NaF at 20 °C. After anodizing to 100 V in the first stage, the specimen was left in the electrolyte for 1200 s. The second stage of anodizing was then started and continued until the voltage reached 200 V.](image)

87
In order to determine whether the reduction in the efficiency of film growth in the solution containing $3.5 \times 10^{-2}$ M sodium fluoride was due to the chemical dissolution of the film, specimens were first anodized in the solution to 100 V. The current was then switched off and the specimens were left in the solution, with stirring maintained, for times from 60 s to 1200 s. The shortest time in the range is similar to the time taken for the voltage to reach 100 V during the previous film growth. The longest time is about 20 times longer. The current was then re-applied and anodizing resumed. Figure 4-2 shows the dependence of the voltage on time for the two periods of anodizing for a specimen immersed in the electrolyte for 1200 s between the two stages of anodizing. This is the longest time of immersion in the range examined. The interruption of anodizing had a very small effect on the film growth for any of the immersion times. The voltage at the start of the second stage of anodizing was about 1 to 2 V lower than the final voltage of the first stage of anodizing, with no significant dependence on the period of interruption. Thus, any loss of film thickness due to the chemical dissolution of the film during the period of interruption of anodizing was negligible. Hence, chemical dissolution of the film can be disregarded as a factor in determining the efficiency of film growth. The decrease in the efficiency of film growth is therefore attributable to the field-assisted ejection of Al$^{3+}$ ions at the film surface. The field-assisted ejection of Al$^{3+}$ ions may be promoted by the adsorption of fluoride ions on the film surface, which replace hydroxyl and boron species and possibly promote the formation of soluble cations, such as AlF$^{2+}$ and AlF$_2^+$ [214, 215].

### 4.2.2 Transmission electron micrograph

Figure 4-3 presents a transmission electron micrograph of an ultramicrotomed cross-section of a specimen that had been anodized to 100 V in 0.1 M ammonium pentaborate solution containing $3.5 \times 10^{-2}$ M sodium fluoride. The distributions of oxygen, aluminium and fluorine are shown in the accompanying elemental maps. A map for boron is not shown due to the potential for interference from carbon contamination, which results in an X-ray energy close to that from boron. However, the results of GDOES examination of the film, which is presented later, showed that that the film contained negligible amounts of boron.
The micrograph in Figure 4-3 reveals an anodic film with a thickness of about 110 nm. The thickness is slightly less than that expected for the usual formation ratio of 1.2 nm V\(^{-1}\) for the growth of anodic films in ammonium pentaborate solution at the present current density and temperature [181]. The reduction in thickness is due to shrinkage of the film during an examination in the transmission electron microscope. Light spots in the film indicate that crystallization of the film had commenced due to exposure to the electron beam. The dark band at the interface between the film and the aluminium substrate is due to the film detaching from the aluminium. The detachment of the film occurred during sectioning of the film by ultramicrotomy. This is not a usual occurrence during sectioning of films formed in fluoride-free ammonium pentaborate solution. The oxygen and aluminium elemental maps indicate that these species are present throughout the films. Furthermore, there is a thin layer containing oxygen beneath the dark band. The fluorine map indicates that fluorine is present in the film above the dark band but is absent from the thin oxygen-containing layer that is attached to the aluminium substrate. The concentration of fluorine is enhanced in the innermost 10 nm of the film thickness above the dark band. This may be an overestimate of the true thickness of the fluorine-rich region, due to the limitations of the spatial resolution of the EDX analysis procedure. The thin oxygen-rich layer beneath the fluoride-rich layer is attributable to the detachment of the film due to the
stress generated during ultramicrotomy. The detachment allows an oxide/hydroxide layer to form on the bared substrate by reaction between the aluminium and the water from which the sections are collected at the rear diamond knife. AlF₃ could be formed at the base of the film and cause film detachment from the substrate which may be assisted by local compressive stresses, since the volume of AlF₃ per mole of aluminium is about 2.7 times greater than that of the aluminium metal and 1.6 times greater than that of amorphous anodic alumina, based on the densities of AlF₃ and Al₂O₃, which are similar about 3.1 g cm⁻³ [32]. Although the detachment of the film formed in the fluoride-containing solution may be due to an inherently weaker bond between the film and the substrate, it is also possible that dissolution of material in the fluoride-rich layer while the ultramicrotomed sections floated on the water behind the edge of the diamond knife. Films could not be detached from specimens by attaching and pulling off the electrical tape. Furthermore, SEM observations of a specimen that had been anodized to 100 V and then scratched through to the substrate revealed only a very localized detachment of small pieces of the film adjacent to the edges of the scratch.

4.2.3 Compositional analysis of films by EDX spectroscopy

In order to determine the amount of fluorine, EDX analysis of the films was carried out on the surface of two specimens anodized in the ammonium pentaborate solution containing 3.5 x 10⁻² M sodium fluoride. One specimen had been anodized to 100 V, the other to 200 V. Measurements for the film formed to 100 V were made at accelerating voltages in the range from 2.5 to 5 kV. The area of analysis was of size 15 μm x 16 μm. From the various measurements, the optimum voltage was considered to be 3 kV. This choice of voltage was made because voltages of 4 and 5 kV resulted in apparently high atomic ratios of Al:O relative to Al₂O₃, which suggested that X-rays were being detected from both the film and the aluminium substrate. An accelerating voltage of 2.5 kV led to a lower concentration of fluorine than at 3.0 kV, which suggested that X-rays were not being generated from the base of the film, where the fluorine-enriched layer is to be found. For the film formed to 200 V, an area of 45 μm x 45 μm was analyzed. A similar exercise of investigating a range of accelerating voltages identified a preferred accelerating voltage of 5 kV. The higher value in comparison with that used for the 100 V film is due to the increased film thickness and hence the increased depth of the fluorine-enriched layer.
Table 4-1 Results of EDX analyses of films formed at 5 mA cm$^{-2}$ in 0.1 M ammonium pentaborate solution containing sodium fluoride at 20 °C

<table>
<thead>
<tr>
<th>NaF concentration</th>
<th>Anodizing voltage</th>
<th>Al (at.%</th>
<th>O (at.%</th>
<th>F (at.%</th>
<th>F:O ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5 x 10$^{-4}$</td>
<td>100</td>
<td>40.7</td>
<td>59.0</td>
<td>0.3</td>
<td>0.005</td>
</tr>
<tr>
<td>3.5 x 10$^{-3}$</td>
<td>100</td>
<td>41.0</td>
<td>47.4</td>
<td>1.6</td>
<td>0.027</td>
</tr>
<tr>
<td>3.5 x 10$^{-2}$</td>
<td>100</td>
<td>40.2</td>
<td>54.4</td>
<td>5.4</td>
<td>0.100</td>
</tr>
<tr>
<td>3.5 x 10$^{-2}$</td>
<td>200</td>
<td>40.3</td>
<td>53.4</td>
<td>6.3</td>
<td>0.118</td>
</tr>
</tbody>
</table>

Figure 4-4 shows the EDX spectra for the preferred analysis conditions and Table 4-1 gives the resulting film compositions. A small peak is evident in each spectrum from carbon contamination, which was disregarded for the analyses.

Figure 4-4  EDX spectra for aluminium specimens that had been anodized at 5 mA cm$^{-2}$ and 20 °C in 0.1 M ammonium pentaborate solution containing (a) 3.5 x 10$^{-4}$ M NaF to 100 V, (b) 3.5 x 10$^{-3}$ M NaF to 100 V, (c) 3.5 x 10$^{-2}$ M NaF to 100 V and (d) 3.5 x 10$^{-2}$ M NaF to 200 V.
The amount of fluoride in the film increased with increasing additions of sodium fluoride to the ammonium pentaborate solution. The small difference between the measured fluorine contents of the two films formed to 100 and 200 V in the solution containing $3.5 \times 10^{-2}$ M sodium fluoride is probably the result of the selection of the accelerating voltage used for the analyses. The atomic concentrations of fluorine in the films were about 0.3, 1.6 and 5.9 % for additions of $3.5 \times 10^{-4}$, $3.5 \times 10^{-3}$ and $3.5 \times 10^{-2}$ M sodium fluoride. The analyses indicate that the films could be composed of units of AlF$_3$ and Al$_2$O$_3$ with an average ratio of approximately 0.005, 0.027 and 0.109 respectively.

4.2.4 Elemental depth profiles by Glow Discharge Optical Emission Spectrometer (GDOES)

Elemental depth profiles determined using GDOES for aluminium, oxygen and boron for a specimen anodized at 5 mA $\text{cm}^{-2}$ to 100 V in 0.1 M ammonium pentaborate solution are presented in Figure 4-5 (a). The figure also included the background intensity measured at the wavelength used for the detection of fluorine in the specimens anodized in the fluoride-containing electrolytes. Furthermore, prior sputtering of aluminium was carried out to ensure that there was no fluorine contaminant present in the instrument from previous uses of the instrument.

The aluminium profile shows an increase in intensity after sputtering for about 11.6 s, which indicates when the aluminium substrate was first exposed following sputtering of the anodic film. The location of the aluminium/film interface is taken as the half-height of the rising edge of the aluminium profile, which occurs after sputtering for about 12.9 s. At this time, the intensity of the oxygen signal reduces to the background level. The intensity of the boron signal is significantly higher during sputtering of the outer part of the film compared with the inner part of the film. The greatly enhanced intensity immediately after the start of sputtering may indicate an increased amount of boron at the film surface. Alternatively, it may be an artefact produced by the initial stabilization of the plasma. The half-height in the trailing edge of the boron intensity occurs after sputtering for about 5.9 s. This is about 46% of the time to sputter through the whole film thickness. It is known from other work that used TEM that boron is located in the outer 40% of the film thickness [182]. The atomic ratio of boron to aluminium in the outer region has been measured previously to be about 0.08 [91].
GDOES elemental depth profiles for aluminium specimens anodized at 5 mA cm\(^{-2}\) in 0.1 M ammonium pentaborate solution at 20 °C (a) to 100 V with no addition of NaF; (b) to 100 V with addition of 3.5 \(\times\) 10\(^{-2}\) M NaF; (c) to 200 V with addition of 3.5 \(\times\) 10\(^{-2}\) M NaF; (d) to 100 V with no addition of NaF followed by to 200 V with addition of 3.5 \(\times\) 10\(^{-2}\) M NaF. The aluminium, oxygen, boron and fluorine intensities were multiplied by factors of 5, 10, 10 and 1 respectively.

Boron is present in the film as an immobile species that resides in the proportion of the film thickness that is formed by the outward migration of Al\(^{3+}\) ions [182]. A slower rate of sputtering in the outer region of the film than in the inner region may account for the small difference in the boron distribution indicated from GDOES and TEM. With respect to this possibility, about three seconds elapsed at the start of sputtering before the oxygen signal rose to a relatively steady level, which suggests an initially slower sputtering rate. The findings of a previous study of the migration rate of a range of incorporated species in barrier-type anodic films on aluminium suggested that the migration rate of a particular species relative to O\(^{2-}\) ions are related to the single bond energy with oxygen [216]. Accordingly, the immobility of boron correlates with a relatively high energy of the B\(^{3+}\)-O\(^{2-}\) bond compared with the Al\(^{3+}\)-O\(^{2-}\) bond [216].
Figure 4-5 (b) shows the elemental profiles for a specimen anodized at 5 mA cm$^{-2}$ to 100 V in 0.1 M ammonium pentaborate solution containing 3.5 x 10$^{-2}$ M sodium fluoride. The aluminium/film interface is reached at a sputtering time of about 11.9 s. The intensity at the wavelength used for detection of boron is at the background level. Hence, the amount of boron within the film is negligible. This may explain the shorter time of sputtering through the film compared with the specimen anodized in the fluoride-free solution (Figure 4-5 (a)). The absence of a boron-containing, outer region of the film indicates that the outwards migrating Al$^{3+}$ ions in the film are ejected to the electrolyte at the film/electrolyte interface. Thus, the film formed at a reduced efficiency, as indicated by the voltage-time response of Figure 4-1, and grew mainly by migration of O$^{2-}$ ions to the aluminium/film interface. The intensity of fluorine is about three times the background level through most of the film thickness, indicating that fluorine is present in the film. Furthermore, a peak in the intensity occurs at the base of the film, indicating an enrichment of fluorine in a thin layer adjacent to the aluminium/film interface. This is consistent with the enrichment of fluorine detected by EDX elemental mapping in Figure 4-3. A small peak also occurs in the aluminium signal at a slightly later time than the time of the fluorine peak. The former peak is possibly associated with the change in the rate of sputtering between the oxide/fluoride film and the aluminium substrate.

Figure 4-5 (c) shows the elemental profiles for a specimen anodized to 200 V in 0.1 M ammonium pentaborate solution containing 3.5 x 10$^{-2}$ M sodium fluoride. The time to sputter to the aluminium/film interface was about 22.0 s. The interface is less sharp than that of the specimens in Figure 4-5 (a and b). This is associated with the greater thickness of the film, which results in a less uniform base of the sputtering crater. Furthermore, examination of a film formed to 200 V indicated that as the anodizing progresses from 100 V to 200 V, the aluminium/film interface develops shallow scallops and the film surface becomes less flat, which appeared to be due to the start of a transition to a porous-film morphology. Through most of the film thickness, the intensity of the fluorine signal was similar to that in the specimen anodized to 100 V (Figure 4-5 (b)). However, the width of the fluorine peak at the aluminium/film interface was about double that of the specimen anodized to 100 V, suggesting an increased thickness of the fluorine-enriched layer or an increased concentration of fluorine within the layer.
Figure 4-5 (d) shows the elemental profiles for a specimen that had been sequentially anodized at 5 mA cm$^{-2}$ first to 100 V in 0.1 M ammonium pentaborate solution and then further anodized to a final voltage of 200 V in 0.1 M ammonium pentaborate solution containing $3.5 \times 10^{-2}$ M sodium fluoride. The aluminium/film interface is located at a sputtering time of about 23.0 s. Boron is present in an outer layer of the anodic film. The intensity of the signal is similar to that of the film formed in the fluoride-free solution (Figure 4-5 (a)). The time to sputter through the boron-containing regions is about 6.0 s, which is close to that for sputtering through the boron-containing region of the film formed in the fluoride-free solution. Thus, the boron that was incorporated into the film in the first period of anodizing, i.e. in the fluoride-free solution, has been retained in the film during the subsequent period of anodizing in the fluoride-containing solution. Since Al$^{3+}$ ions are ejected to the electrolyte during anodizing in the latter solution no fresh alumina is formed above the boron-containing layer. Fluoride is present throughout the film thickness. However, no peak in the intensity is present at the base of the anodic film. In the second stage of anodizing at 60% efficiency, the film is forming by the inward migration of O$^{2-}$ ions to the aluminium/film interface. Hence, the fluoride ions must migrate about twice as fast as the O$^{2-}$ ions in order to reach the aluminium/film interface, as shown in the schematic diagram of Figure 4-6, the rate relative to O$^{2-}$ ions is similar to those measured for fluoride ions in tantalum and titania films. No peak in the fluorine intensity occurs in the GDOES profile since the inward migrating fluoride ions have only just reached the bottom of the film. The presence of immobile boron species in the outer layer appears to have no influence on the migration of fluoride ions to the inner, boron-free region of the film.

Amorphous anodic oxides on valve metals, such as aluminium, tantalum and niobium, grow by counter migration of metal ions and oxygen ions [217]. The transport numbers of the respective ions depend upon the particular anodic oxide [217]. Migration involves the movement of ions over distances of atomic dimensions, which conserves the order of metal and oxygen species, apart from a small amount of diffusional mixing [49, 218]. The oxides can show a large degree of ductility during their growth [219, 220] due to the high ionic flux that involves practically simultaneous movements of all of the ions in the oxide [217]. It is therefore suggested that in the present films fluoride ions migrate through a labile atomic arrangement that is created by the weakening or breaking of bonds between Al$^{3+}$ and O$^{2-}$ ions. Thus, migration of fluoride ions is linked to the migration of Al$^{3+}$ and O$^{2-}$.
ions, and would not be expected to occur in the absence of film growth. This expectation is in accord with the results of a study of the migration of chloride ions in anodic alumina, which showed that their migration did not occur in the absence of film growth [205].

Figure 4-6 Schematic diagram showing (a) the film formed to 100 V in ammonium pentaborate solution and (b) the film formed by further anodizing to 200 V in ammonium pentaborate solution containing $3.5 \times 10^{-2}$ M NaF.

Since the fluoride ions migrate inward at about twice the rate of $\mathrm{O}^{2-}$ ions, approximately half of the fluorine detected by EDX analysis is associated with the fluorine-rich layer at the film base. Thus, it can be estimated from the atomic concentration of oxygen in anodic alumina and the measured atomic ratio of fluorine to oxygen that a thickness of $\mathrm{AlF}_3$ of about 5 nm can be formed at the base of the film following anodizing to 100 V. The measured rate of fluoride migration is significantly greater than the rate predicted by extrapolation of the dependence of the migration rate of chloride, bromide and iodide ions on the ionic radius, which suggested a migration rate only about 10% higher than that of $\mathrm{O}^{2-}$ ions [216].

4.2.5 Scanning electron microscopy

The voltage-time curve of Figure 4-1 (b) indicated the formation of a porous anodic film when the concentration of sodium fluoride was $3.5 \times 10^{-1}$ M. This was confirmed by examination of the film surface and cross-sections by SEM. Figure 4-7 (a) shows the
general appearance of the surface at low magnification. The surface reveals a porous film that appears to be non-uniformly degraded by chemical dissolution during anodizing resulting in regions of different film thickness. The porosity is more clearly revealed in the images at increased magnification, shown in Figure 4-7 (b, and c), which depict the thicker and thinner regions displayed in Figure 4-7 (a). Figure 4-7 (b) shows the thicker region displayed in Figure 4-7 (a), with pores that range in size from a few nanometer to a few tens of nanometers in diameter. Figure 4-7 (c) shows a degraded film surface, where the cellular film structure appears to have partially collapsed by thinning of the cell walls. The cross-section of the specimen, shown in Figure 4-7 (d), reveals the typical morphology of a porous alumina film. The diameter of the pores appears to be in the range from about 10 to 20 nm. The surface of the film has been degraded by chemical dissolution in the electrolyte, which may have also led to an increased pore diameter.

Figure 4-7 Scanning electron micrographs of the surface of an aluminium specimen that had been anodized for 600 s at 5 mA cm\(^{-2}\) in 0.1 M ammonium pentaborate solution, containing 3.5 x 10\(^{-2}\) M NaF, at 20 °C. (a) General view of the surface. (b,c) Increased magnification images of regions in (a). (d) Cross-section of the specimen.
It is not possible to identify which region of the film was specimen by the cross-sectioning since the regions were of small area and randomly distributed across the specimen surface. The film in Figure 4-7 (d) is about 775 nm thick. In comparison, the charge passed during anodizing was sufficient to oxidize about 1040 nm of aluminium. The difference in the thicknesses is further evidence of dissolution of the film since the thickness of a porous film is normally similar to or exceeds the thickness of the oxidized aluminium.

4.3 Conclusions

1. Anodizing of aluminium in ammonium pentaborate solution containing additions of sodium fluoride leads to incorporation of fluoride ions into the anodic film.

2. The incorporated fluoride ions migrate inwards at about twice the rate of O\textsuperscript{2-} ions. Consequently, a fluoride-enriched layer is formed at the base of the film.

3. Fluoride ions can promote the field-assisted ejection of Al\textsuperscript{3+} ions from the surface of the anodic film, thereby reducing the efficiency of film growth.

4. Sufficient additions of fluoride ions result in the growth of a porous anodic film under a low voltage.
5 Influence of fluorozirconic acid on sulphuric acid anodizing of aluminium

5.1 Introduction

Chromium (VI)-free conversion treatments that include fluorotitanic and fluorozirconic acids in the bath formulations have been developed for aluminium alloys [197, 199-203]. The resultant coatings comprise chromium (III) (if present in the bath), titanium and zirconium fluorides, oxides and hydroxides, which constitute the main part of the coating thickness, and a comparatively thin layer of aluminium oxyfluoride next to the substrate. In comparison with the findings from the relatively numerous studies of conversion coatings produced using fluoroacids, very little information is available on the use of fluoroacids in anodizing of aluminium and aluminium alloys. One study has been made of anodizing aluminium and aluminium alloys at a constant current density in fluoroboric acid solutions at temperatures ranging from 0 to 30 °C [12]. Porous films were formed, with a pore size and population density that depended on the concentration and temperature of the fluoroboric acid solution and the time of anodizing. However, the information provided on the morphology and composition of the films was very limited and the role of the fluoroacid in the growth of the film was not considered. More recent studies examined the influence of ammonium hexafluorosilicate [13] and ammonium fluoride [13, 14], additions to oxalic acid on the formation of porous anodic films on aluminium.

The effect of hexafluorosilicate ions was more pronounced than that of fluoride ions, suggesting that Si-F bonds may be broken under the high electric field to generate free fluoride ions [13]. Increasing the concentration of the fluorine species in the electrolyte progressively reduced the barrier layer thickness [14] and also the voltage during anodizing under a constant current [13]. It was suggested that fluoride additions led to a microporous outer region of the barrier layer [14]. Furthermore, fluorine was detected at the base of the inner, non-porous region [14]. It was proposed that the incorporated fluoride generated a negative space charge that promoted the injection of Al$^{3+}$ ions into the film thereby increasing the current density under a particular applied voltage [14].
5.2 Results and Discussion

5.2.1 Current density-time curves and film morphologies

The effects of fluorozirconic acid additions (Table 5-1) on the current density-time curves during anodizing of aluminium in 0.1 M sulphuric acid for 1200 s at a constant voltage of 22 V are presented in Figure 5-1 (a) and (b) for temperatures of 0 and 20 °C, respectively. Additions of 0.1, 0.5 and 1.0 wt.% of fluorozirconic acid increased the current density at both temperatures relative to the control specimens anodized in the fluoroacid-free electrolyte. A peak current density occurred for all specimens immediately on the application of the voltage due to the rapid growth of a barrier layer under a very high initial electric field. The current density then rapidly decreased to a minimum value due to the reduction in the field as the film thickened. The inset in Figure 5-1 (a) shows the trends in the current density during the first 100 s of anodizing. For the control specimens, a steady current density was subsequently achieved. In contrast, the presence of the fluoroacid led to a second peak followed by a slow decline towards a steady value.

Table 5-1. Concentrations of fluorozirconic acid (FZ), total fluorine and free fluoride added to 0.1 M sulphuric acid electrolyte.

<table>
<thead>
<tr>
<th>FZ addition to 0.1 M H₂SO₄ (wt. %)</th>
<th>FZ concentration</th>
<th>Total fluorine concentration</th>
<th>Free fluoride</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>2.24 x 10⁻²</td>
<td>1.34 x 10⁻²</td>
<td>3.46 x 10⁻⁵</td>
</tr>
<tr>
<td>0.5</td>
<td>1.12 x 10⁻²</td>
<td>6.72 x 10⁻²</td>
<td>1.73 x 10⁻³</td>
</tr>
<tr>
<td>1.0</td>
<td>2.24 x 10⁻²</td>
<td>1.34 x 10⁻¹</td>
<td>3.46 x 10⁻⁷</td>
</tr>
</tbody>
</table>

The effect of the concentration of sulphuric acid on the anodizing behaviour was investigated using a 1.0 M sulphuric acid solution containing 0.1 wt.% fluorozirconic acid. Films were formed for 1200 s at either 0 or 20 °C. The resultant current density-time curves are shown in Figure 5-1 (c), which also includes the curves for the fluoroacid-free solution. Similarly to the observations made with the 0.1 M sulphuric acid, the current density was enhanced by the fluoroacid, with the effect decreasing with increasing anodizing time.

Figure 5-2 shows scanning electron micrographs of the resultant film surfaces. Porous surfaces were obtained at 0 °C for all fluorozirconic acid concentrations, and also at 20 °C with 0.1 wt.% fluorozirconic acid. However, the addition of 0.5 and 1.0 wt.%
fluorozirconic acid resulted in a collapsed cell structure. Micrographs of cross-sections of the films, which were prepared by ultramicrotomy, are shown in Figure 5-3. The film thickness measured from the micrographs and the charge density passed in forming the films are listed in Table 5-2. The increments in the film thickness due to additions of 0.1, 0.5 and 1.0 wt.% fluorozirconic acid (i.e. (thickness of test specimen – the thickness of control specimen) / thickness of control specimen) were 1.64, 6.64 and 7.95 at 0 °C, and 0.95, 1.78 and 2.09 at 20 °C. Scanning electron micrographs of the surfaces and cross-sections of the films formed using 1.0 M sulphuric acid containing 0.1 wt.% fluorozirconic acid (not shown here), revealed an intact porous structure at the film surface at 0 °C. At 20 °C, the surface structure was partially degraded; cross-sections revealed that the degradation was limited to the film surface. The increments in film thickness due to the fluoroacid were 1.30 and 0.25 at 0 and 20 °C, respectively.
Figure 5-1. Current-density-time curves for aluminium anodized at 22 V in 0.1 M H₂SO₄ at (a) 0 °C and (b) 20 °C. Curves A and E – control specimens anodized without fluorozirconic acid; curves B and F – 0.1 wt.% fluorozirconic acid; curves C and G – 0.5 wt.% fluorozirconic acid; curves D and H – 1.0 wt.% fluorozirconic acid. (c) Anodized in 1.0 M H₂SO₄; curves A and C – control specimens anodized without fluorozirconic acid at 0 and 20 °C, respectively; curves B and D – 0.1 wt.% fluorozirconic acid at 0 and 20 °C, respectively.
Figure 5-2. Scanning electron micrographs (backscattered electrons) of the surfaces of anodic films formed on aluminium at 22 V in 0.1 M H$_2$SO$_4$ at 0 °C (top row) and at 20 °C (bottom row). A and E – control specimens anodized without fluorozirconic acid; B and F – 0.1 wt.% fluorozirconic acid; C and G – 0.5 wt.% fluorozirconic acid; D and H – 1.0 wt.% fluorozirconic acid.

Figure 5-3. Scanning electron micrographs (secondary electron electrons) of the cross-sections of anodic films formed on aluminium at 22 V in 0.1 M H$_2$SO$_4$ at 0 °C (top row) and at 20 °C (bottom row). A and E – control specimens anodized without fluorozirconic acid; B and F – 0.1 wt.% fluorozirconic acid; C and G – 0.5 wt.% fluorozirconic acid; D and H – 1.0 wt.% fluorozirconic acid.

The thickness values of films that exhibited collapsed cell structures are shown in bold type in Table 5-2. Additions of 0.1, 0.5 and 1.0 wt.% fluorozirconic acid to 0.1 M sulphuric acid increased the charge density relative to the control specimen by factors of
about 2.5, 7.5 and 8.3 at 0 °C, respectively, and by factors of about 2.1, 6.0 and 12.0 at 20 °C. The ratio of the film thickness to the charge density was in the range 0.45 to 0.49 μm cm⁻² for specimens anodized at 0 °C, including the control specimens. The similarity of the values suggests a negligible loss of film thickness due to chemical dissolution in the presence of the fluorozirconic acid. At 20 °C, the ratio reduced to 0.40, 0.20 and 0.11 μm cm⁻² as the concentration of fluorozirconic acid was increased, indicating significant film thinning with additions of 0.5 and 1.0 wt.% fluorozirconic acid. The ratios of the film thickness to the charge density for the specimens anodized in 1.0 M sulphuric acid containing 0.1 wt.% fluorozirconic acid were similar to those of the respective control specimens, showing that the loss of film thickness due to film dissolution was insignificant in the fluoroacid-containing electrolyte.

Table 5-2. Thicknesses of films, determined by SEM, and charge density passed for anodizing of aluminium for 1200 s at 22 V in 0.1 M H₂SO₄ containing different concentrations of fluorozirconic acid (FZ) at 0 °C and 20 °C. The thicknesses in bold type indicate a collapsed porous structure at the film surface.

<table>
<thead>
<tr>
<th></th>
<th>FZ (wt. %)</th>
<th>0.1 M H₂SO₄</th>
<th>1.0 M H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0 °C</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film thickness (μm)</td>
<td>0.22 ± 0.02</td>
<td>0.58 ± 0.02</td>
<td>1.68 ± 0.02</td>
</tr>
<tr>
<td>Charge density (C/cm²)</td>
<td>0.486</td>
<td>1.232</td>
<td>3.646</td>
</tr>
<tr>
<td>Ratio (μm cm²/C)</td>
<td>0.45</td>
<td>0.47</td>
<td>0.46</td>
</tr>
<tr>
<td><strong>20 °C</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film thickness (μm)</td>
<td>0.94 ± 0.01</td>
<td>2.02 ± 0.01</td>
<td>2.61 ± 0.05</td>
</tr>
<tr>
<td>Charge density (C/cm²)</td>
<td>2.147</td>
<td>4.607</td>
<td>12.837</td>
</tr>
<tr>
<td>Ratio (μm cm²/C)</td>
<td>0.44</td>
<td>0.40</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Figure 5-4 presents bright field transmission electron micrographs of films formed on 300 and 1200 s, in 0.1 M sulphuric acid containing 0.1 wt.% fluorozirconic acid at 0 °C. The films are 194 ± 8 and 609 ± 19 nm thick, respectively. The thicknesses indicate average film growth rates of about 0.64 and 0.51 nm s⁻¹. The slower rate measured for the longer time of anodizing is consistent with the reducing current density observed in the voltage-time curve of Figure 5-1 (a). The latter growth rate compares satisfactorily with a rate of 0.48 nm s⁻¹ calculated using the film thickness of Table 5-2 determined from the scanning electron micrograph of the film cross-section. The films reveal some damage due to the
sectioning by ultramicrotomy using a diamond knife. However, a typical porous structure is evident with mainly unbranched pores. The barrier layers in the films were about 20 nm thick, indicating a formation ratio of about 0.9 nm V⁻¹, consistent with values reported in the literature for anodizing in sulphuric acid [221].

![Figure 5-4](image)

Figure 5-4. Bright-field transmission electron micrographs of ultramicrotomed cross-sections of aluminium anodized at 22 V for (a) 300 s, and (b) 1200 s, in 0.1 M H₂SO₄ containing 0.1 wt.% fluorozirconic acid at 0 °C.

Table 5-3. Thicknesses of films and charge density passed for anodizing of aluminium at 22 V for 1200 s in 0.1 M H₂SO₄ containing different concentrations of sodium fluoride at 0 °C and 20 °C. The thickness value in bold type is a film with a collapsed porous structure at the film surface. No measurements were made for 3.5 x 10⁻³ M NaF at 20 °C due to severe film dissolution.

<table>
<thead>
<tr>
<th>NaF (M)</th>
<th>0</th>
<th>3.5 x 10⁻³</th>
<th>3.5 x 10⁻²</th>
<th>3.5 x 10⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 °C</td>
<td>Film thickness (µm)</td>
<td>0.22 ± 0.02</td>
<td>0.91 ± 0.01</td>
<td>1.65 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Charge density (C/cm²)</td>
<td>0.486</td>
<td>2.026</td>
<td>3.096</td>
</tr>
<tr>
<td></td>
<td>Ratio (µm cm²/C)</td>
<td>0.45</td>
<td>0.44</td>
<td>0.54</td>
</tr>
<tr>
<td>20 °C</td>
<td>Film thickness (µm)</td>
<td>0.94 ± 0.01</td>
<td>1.28 ± 0.02</td>
<td><strong>2.69 ± 0.01</strong></td>
</tr>
<tr>
<td></td>
<td>Charge density (C/cm²)</td>
<td>2.147</td>
<td>3.34¹</td>
<td>10.175</td>
</tr>
<tr>
<td></td>
<td>Ratio (µm cm²/C)</td>
<td>0.44</td>
<td>0.38</td>
<td>0.26</td>
</tr>
</tbody>
</table>
Sodium fluoride had a generally similar effect on the anodizing curves as the fluoroacids: the charge density at 0 °C increased progressively with additions of 3.5 x 10^{-3}, 3.5 x 10^{-2} and 3.5 x 10^{-1} M sodium fluoride by factors of about 4.2, 6.4 and 8.8 at 0 °C (Table 5-3). At 20 °C, only the first two additions were made, which gave increases in the charge density by factors of about 1.3, 1.6 and 4.7. The highest addition was excluded from examination because of severe film dissolution. The films retained a porous surface structure for additions of 3.5 x 10^{-3} and 3.5 x 10^{-2} M at 0 °C and to 3.5 x 10^{-3} M at 20 °C. The disintegration of the porous structure due to chemical dissolution occurred for 3.5 x 10^{-1} M at 0 °C, and the collapse of the structure at 3.5 x 10^{-2} M at 20 °C. The ratio of the film thickness to the charge density was in the range 0.44 to 0.54 nm cm^2 mC^{-1} at 0 °C but was reduced by film dissolution to the range 0.38 to 0.26 nm cm^2 mC^{-1} at 20 °C. Increasing additions of sodium fluoride resulted in increments of the film thickness of 3.14, 6.49 and 8.05 at 0 °C for additions from 3.5 x 10^{-3} to 3.5 x 10^{-1} M sodium fluoride, respectively, and of 0.36, 1.86 at 20 °C for additions of 3.5 x 10^{-3} and 3.5 x 10^{-2} M sodium fluoride.

5.2.2 Film compositions: EDX spectroscopy

EDX analyses were carried out of the films formed for 300 s at 0 and 20 °C with additions of either fluorozirconic acid or sodium fluoride. The analyses were made using accelerating voltages in the range 3 to 6 kV in an area on the specimen surface of size 20 x 20 μm. Aluminium, oxygen, sulphur and fluorine were present in the films. No sodium, originating from sodium fluoride, or zirconium (assessed from the Zr Lα line), originating from the fluorozirconic acid, was detected. Later RBS analysis confirms that the amount of incorporated zirconium was negligible. The results of averages of typically three analyses of each specimen are given in Table 5-4. A small peak from carbon contamination was disregarded in determining the film compositions. The atomic ratios of S: Al in the films formed with additions of 0.1, 0.5 and 1.0 wt.% of fluorozirconic acid were in the range 0.05 to 0.07. They did not depend significantly on either the temperature of the electrolyte or the concentration of the fluoroacid. The S: Al ratio is consistent with a ratio of about 0.07 to 0.08 that has been reported in films formed using a higher sulphuric acid concentration of 3 wt.% at 0 °C [222].
Table 5-4. EDX analyses of anodic films formed on aluminium for 300 s at 22 V in 0.1 M H$_2$SO$_4$ or 1.0 M H$_2$SO$_4$ containing different concentrations of fluorozirconic acid (FZ) or sodium fluoride at 0 °C and 20 °C. (n.d. = not determined due to low kV required for analysis)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>0 °C F</th>
<th>0 °C S</th>
<th>0 °C F:Al</th>
<th>0 °C S:Al</th>
<th>20 °C F</th>
<th>20 °C S</th>
<th>20 °C F:Al</th>
<th>20 °C S:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M H$_2$SO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 wt.% FZ</td>
<td>2.6</td>
<td>2.2</td>
<td>0.06</td>
<td>0.06</td>
<td>2.7</td>
<td>2.1</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>0.5 wt.% FZ</td>
<td>4.9</td>
<td>2.4</td>
<td>0.14</td>
<td>0.07</td>
<td>5.3</td>
<td>2.2</td>
<td>0.14</td>
<td>0.06</td>
</tr>
<tr>
<td>1.0 wt.% FZ</td>
<td>5.8</td>
<td>2.4</td>
<td>0.16</td>
<td>0.07</td>
<td>8.9</td>
<td>1.9</td>
<td>0.25</td>
<td>0.05</td>
</tr>
<tr>
<td>3.5 x 10^{-3} M NaF</td>
<td>1.7</td>
<td>n.d.</td>
<td>0.04</td>
<td>n.d.</td>
<td>1.0</td>
<td>2.1</td>
<td>0.03</td>
<td>0.06</td>
</tr>
<tr>
<td>3.5 x 10^{-2} M NaF</td>
<td>3.2</td>
<td>2.7</td>
<td>0.08</td>
<td>0.07</td>
<td>2.1</td>
<td>2.2</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>3.5 x 10^{-1} M NaF</td>
<td>12.9</td>
<td>1.9</td>
<td>0.37</td>
<td>0.06</td>
<td><strong>7.4</strong></td>
<td><strong>2.2</strong></td>
<td><strong>0.21</strong></td>
<td><strong>0.06</strong></td>
</tr>
<tr>
<td>1.0 M H$_2$SO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 wt.% FZ</td>
<td>1.0</td>
<td>3.5</td>
<td>0.03</td>
<td>0.10</td>
<td>0.7</td>
<td>3.5</td>
<td>0.02</td>
<td>0.10</td>
</tr>
</tbody>
</table>

The average S: Al ratio and sulphur concentration for all of the specimens anodized using fluoroacids were 0.060 and 2.2 at.%, respectively. S: Al ratios within the previous range were also obtained with additions of sodium fluoride. For films formed with 0.1, 0.5 and 1.0 wt.% fluorozirconic acid additions, the F: Al ratio increased as the amount of fluorozirconic acid was increased. At 0 °C, the F:Al ratios were 0.06, 0.14 and 0.16 for 0.1, 0.5 and 1.0 wt.%, respectively, with corresponding fluorine concentrations of 2.6, 4.9 and 5.8 at.%, and 0.07, 0.14 and 0.25 at 20 °C, with corresponding fluorine concentrations of 2.7, 5.3 and 8.9 at.%. Thus, the F: Al ratio was enhanced by a factor of 2.7 and 3.6 at 0 and 20 °C, respectively, as the fluoroacid concentration was increased from 0.1 to 1.0 wt.%. The results suggest that the effect of the temperature on the F: Al ratio in the films formed was comparatively small.

Figure 5-5 shows the relationship between the current density averaged over the 300 s time of anodizing and the measured F: Al ratio in films formed at 0 and 20 °C in the electrolytes containing fluorozirconic acid and sodium fluoride. The data were fitted by linear relationships, with the gradient at 0 °C being lower than those at 20 °C. Thus, a given fluoride added to the electrolyte causes a greater increase in the current density at 20 °C than at 0 °C.
The S: Al ratio in the films formed in the 1 M sulphuric acid electrolytes for times of 300 s was increased to about 0.10, compared with values of about 0.06 in the electrolytes containing 0.1 M sulphuric acid (Table 5-4). The ratio is in reasonably good agreement with previous reports of S: Al ratios in films formed in sulphuric acid under similar conditions [13, 143]. The fluorine contents of the films were about 1.0 and 0.7 at.% at 0 and 20 °C, respectively. The respective F: Al ratios were about 0.03 and 0.02, which are about 50 and 30% of those measured in the films formed in 0.1 M sulphuric acid. The film formed at 20 °C for 300 s was also analyzed using a range of accelerating voltages of the electron beam. The detected concentration of fluorine decreased from 0.7 at.% at 5 kV, to 0.5 at.% at 10 kV, and to 0.4 at.% at 15 kV. The O: Al was monitored to ensure that the X-rays were detected only from the film. Considering that a higher acceleration voltage results in increased beam penetration, the results indicate a reduction in the fluorine concentration with increasing depth in the film. In contrast, no significant change occurred in the sulphur concentration.

![Graph showing relationship between F:Al ratio and average current density](image)

Figure 5-5. Relationship between the F: Al atomic ratio in the film and the average current density during anodizing of aluminium at 22 V for 300 s, in 0.1 M H₂SO₄ containing either fluorozirconic acid (FZ) or sodium fluoride (NaF) additions at 0 and 20 °C. The F:Al ratios are taken from Table 4 for specimens anodized with 0.1, 0.5 and 1.0 wt.% fluorozirconic acid and with 3.5 x 10⁻³, 3.5 x 10⁻² and 3.5 x 10⁻¹ M sodium fluoride. (▲ FZ 20 °C, ■ FZ 0 °C, ● NaF 20 °C, ★ NaF 0 °C)
The F: Al ratio was also increased by increasing the concentration of sodium fluoride at 20 °C, with ratios of 0.03, 0.06 and 0.21 for additions of $3.5 \times 10^{-3}$, $3.5 \times 10^{-2}$ and $3.5 \times 10^{-1}$ M sodium fluoride, respectively (Table 5-4). The respective fluorine concentrations were 1.0, 2.1 and 7.4 at.%. The analysis of fluorine for a sodium fluoride concentration of $3.5 \times 10^{-3}$ M required the use of lower electron beam energy to avoid significant interference from the aluminium substrate. This precluded measurement of the sulphur concentration.

The O: Al ratio was similar for all specimens anodized in the presence of fluoroacids and sodium fluoride, with an average value 1.50 and a range from 1.40 to 1.63. A typical film formed using a fluorozirconic acid has an S: Al ratio of about 0.06 and an Al: F ratio of about 0.1. The ratios suggest an average composition of approximately $\text{Al}_2\text{O}_3\cdot0.04\text{Al}_2(\text{SO}_4)_3\cdot0.07\text{AlF}_3$.

In order to determine the distribution of fluorine, EDX analyses were also made at three locations in a cross-section of a film formed on 1200 s at 20 °C in the electrolyte containing 1.0 wt.% fluorozirconic acid. This specimen was chosen because the film was relatively thick, about 2.9 μm. The analyses were made in rectangular areas of size about 6 μm x 0.3 μm. The areas were located within the outer half of the film, in the middle of the film and within the inner half of the film. The O: Al atomic ratio was close to 1.5 in all of the areas, which confirmed that no drift occurred during the analyses. The analyses were carried out at least twice, using different regions of the cross-section. The results are shown in Table 5-5. The fluorine concentration decreased by about 28 % between the outer half of the film and the inner half of the film, whereas the sulphur concentration increased by about 36%. The decrease in the fluorine concentration with depth correlates with the decrease in the current density during film growth (Figure 5-1(b)). The increase in the sulphur concentration may be a consequence of a reduced concentration of fluorine species in the electrolyte within the pores that enables an increase in incorporation of sulphate ions into the film.

### 5.2.3 Film compositions: GDOES

Elemental depth profiles in the anodic films were obtained by GDOES in order to demonstrate the presence of fluorine throughout the thicknesses of films formed on 300 s, thereby complementing the EDX analysis presented previously in Table 5-4. The profiling was restricted to films formed at 0° C.
Figure 5-6. GDOES elemental profiles of aluminium anodized at 22 V for 300 s in 0.1 M H$_2$SO$_4$ at 0 °C containing (a) 0.1, (b) 0.5 and (c) 1.0 wt.% fluorozirconic acid. The aluminium, oxygen, boron and fluorine intensities were multiplied by factors of 5, 10, 10 and 1 respectively.

Results are presented in Figure 5-6 for the films formed with different concentrations of fluorozirconic acid. The aluminium/film interface coincides with the decline of the oxygen
intensity and the rise of the aluminium intensity as sputtering of the substrate commences. The times required to sputter through the films formed using 0.1, 0.5 and 1.0 wt.% fluorozirconic acid were about 37, 68 and 98 s, respectively, correlating with an increasing thickness with increasing additions of fluorozirconic acid. Fluorine was present throughout the thickness of each film. The fluorine signal intensity increased with increase in the concentration of fluorozirconic acid. The signal included background noise, which was estimated from analysis of a control specimen formed in a fluoroacid-free electrolyte. The noise was estimated at about 50% of the total signal intensity of the specimen anodized with 0.1 wt.% fluorozirconic acid. The fluorine analyses by GDOES are in qualitative agreement the EDX analyses, which showed that the fluorine concentration doubled between additions of 0.1 and 1.0 wt.% fluorozirconic acid. The fluorine appeared to be distributed uniformly through most of the film thickness, with apparently no depletion with depth, contrary to findings of EDX analysis of thicker films formed for 1200 s (Table 5-5).

Table 5-5. EDX analyses of a cross-section of an anodic film formed on aluminium for 1200 s at 22 V in 0.1 M H$_2$SO$_4$ containing 1.0 wt.% fluorozirconic acid 20 °C.

<table>
<thead>
<tr>
<th></th>
<th>Outer region</th>
<th>Middle region</th>
<th>Inner region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis 1 F (at.%)</td>
<td>7.9</td>
<td>5.7</td>
<td>5.0</td>
</tr>
<tr>
<td>Analysis 1 S (at.%)</td>
<td>1.5</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Analysis 2 F (at.%)</td>
<td>6.5</td>
<td>5.5</td>
<td>5.4</td>
</tr>
<tr>
<td>Analysis 2 S (at.%)</td>
<td>1.9</td>
<td>1.9</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The absence of depletion is probably a consequence of faster diffusion of fluorine in the pores of the thinner films analyses by GDOES, and possibly also of changes in the sputtering rate of the film during profiling. Sulphur was present throughout most of the thickness of the films. The fluorine signal extended beyond the sulphur signal, which indicates the presence of a sulphur-free, fluorine-containing layer at the base of the films. Optical emission intensities at the wavelength for zirconium (Figure 7-8) were at the background level, indicating negligible amounts of zirconium in the films.
5.2.4 Film compositions: RBS

The zirconium content in a film formed on 300 s, in 0.1 M sulphuric acid containing 0.1 wt.% fluorozirconic acid at 0 °C was measured by RBS, which is sensitive to the presence of heavy elements in a light matrix.

The resultant spectra revealed yields from oxygen, aluminium and sulphur, as shown in Figure 5-7. Comparison with a control specimen, anodized in the absence of fluoroacid, showed that only a pile-up background signal occurred in the energy range expected for zirconium in the film. The upper limit on the Zr: Al atomic ratio was $5 \times 10^{-5}$. The S: Al atomic ratio was about 0.06 in agreement with the results of the EDX analyses. The upper limit on the Zr/S ratio was about $8 \times 10^{-4}$. The Zr/S ratio was, therefore, lower by a factor $\geq 2.8$ than the molar ratio of fluorozirconate ions to sulphate ions in the electrolyte ($2.24 \times 10^{-3}$). The efficiency of anodizing was evaluated from the ratio of the charge due to the Al$^{3+}$ ions in the film (2.76 C cm$^{-2}$) and the charge passed in the anodizing cell (4.02 C cm$^{-2}$). The latter is consumed by oxidizing aluminium, with negligible contributions from side reactions, such as oxygen evolution. The charge ratio indicated that the film formed at an efficiency of about 0.69. Films on control specimens anodized in fluoroacid free electrolytes at 0 and 20 °C formed at efficiencies of 0.63 and 0.64, respectively. The results
suggest that the fluoroacid had negligible influence on the efficiency of oxidation of the aluminium and that dissolution of the film was also negligible. In contrast, it was reported previously that the efficiency of oxidation of the aluminium was reduced progressively by increasing additions of ammonium hexasilicate or ammonium fluoride to oxalic acid [13]. After anodizing for 80 min, at a temperature of 17 °C, and an ammonium hexasilicate concentration of 2.5 mM, the efficiency was about 0.5 and reduced to about 0.1 at a concentration of 10 mM. The origin of the low efficiency was unexplained.

5.2.5 Dissolution rates of films

In order to determine the effect of the concentration of fluorozirconic acid on the chemical dissolution rate, films were formed at 22 V for 1200 s, in 0.1 M sulphuric acid containing either 0.1 or 1.0 wt.% fluorozirconic acid at 0 and 20 °C. The specimens were then left immersed in the electrolyte without application of any voltage for different times to allow chemical dissolution to proceed. Six immersion times were selected for each anodizing condition. The specimens were then rinsed in deionized water and re-anodized at 5 mA cm⁻² in 0.1 M ammonium pentaborate solution at 20 °C and the voltage surge at the start of anodizing was measured. The thickness of the barrier layer was then calculated from the voltage surge using a ratio of 0.9 nm V⁻¹, as suggested by the previous TEM examination of films. Figure 5-8 shows the dependence of the barrier layer thickness on the immersion time. The results indicate a linear relationship between the barrier layer thickness and the immersion time. The dissolution rates determined from the best-fit lines to the data are given in Table 5-6.

Table 5-6. Dissolution rates of the barrier layer in 0.1 M sulphuric acid containing either 0.1 or 1.0 wt.% fluorozirconic acid (FZ) at 0 and 20 °C.

<table>
<thead>
<tr>
<th>FZ (wt.%)</th>
<th>Temperature (°C)</th>
<th>Dissolution rate (nm s⁻¹)</th>
<th>Intercept (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0</td>
<td>2.3 x10⁻⁴</td>
<td>19.5</td>
</tr>
<tr>
<td>0.1</td>
<td>20</td>
<td>2.0 x10⁻⁴</td>
<td>20.1</td>
</tr>
<tr>
<td>1.0</td>
<td>0</td>
<td>2.5 x10⁻⁴</td>
<td>18.3</td>
</tr>
<tr>
<td>1.0</td>
<td>20</td>
<td>2.3 x10⁻⁴</td>
<td>18.2</td>
</tr>
</tbody>
</table>

The line intercepts show that the barrier layer was initially between 18 to 20 nm thick, consistent with the measurement of the barrier layer thickness by TEM. Between 0 to 20 °C, the dissolution rates increased by factors of 8.7 and 9.2 in the solutions containing 0.1 and 1.0 wt.% fluorozirconic acid, respectively. Assuming an Arrhenius relation for the
dissolution rate constant, activation energies of about 67 and 77 kJ mol\(^{-1}\) are indicated for the respective solutions.

![Graph](image)

Figure 5-8 Relationship between the barrier layer thickness and the time of immersion in 0.1 M H\(_2\)SO\(_4\) with addition of (a) 0.1 % fluorozirconic acid at 0 °C; (b) 0.1 % fluorozirconic acid at 20 °C; (c) 1.0 % fluorozirconic acid at 0 °C; 1.0 % fluorozirconic acid at 20 °C. Each specimen was first anodized at 22 V in the same electrolyte for 1200 s.

Increasing the concentration of fluorozirconic acid from 0.1 to 1.0 wt.% increased the dissolution rates by factors of 10.9 and 11.5 at 0 and 20 °C, respectively. After anodizing for 1200 s, thickness losses of 0.3 and 2.4 nm at 0 and 20 °C, respectively are predicted in the solution containing 0.1 wt.% fluorozirconic acid, and 3.0 and 27.6 nm in the solution containing 1.0 wt.% fluorozirconic acid. The thickness of cell walls is estimated to be about 17 nm for an anodizing voltage of 22 V. The thickness loss for anodizing in the presence of 1.0 wt% of fluorozirconic acid at 20 °C is consistent with the observed collapse of the porous structure at the film surface.

The voltage surges at the start of re-anodizing of specimens in ammonium pentaborate solution were about 17.8 and 18.4 V for specimens anodized in the presence of 0.1 wt.% fluorozirconic acid at 0 and 20 °C, respectively, and 17.5 and 15.5 V for specimens anodized in the electrolyte containing 1.0 wt.% fluorozirconic acid. The difference in the surge voltages may be due to the differences in the film compositions, which affect the
magnitude of the electric field required for film growth. Furthermore, chemical dissolution of the barrier layer at the termination of anodizing and prior to rinsing of the specimen in de-ionized water may have a significant influence on the voltage surge at 20 °C for the electrolyte containing 1.0 wt.% fluorozirconic acid. For instance, from the measured chemical dissolution rate, a loss of barrier layer thickness of about 1.4 nm is predicted to be possible in 60 s. For other electrolyte conditions, chemical dissolution is expected to be comparatively negligible.

5.2.6 Film porosity

The porosity of the films was determined from the slopes of the voltage-time curves during re-anodizing at 5 mA cm\(^{-2}\) in 0.1 M ammonium pentaborate solution at 20 °C [190], which results in thickening of the barrier layer. The calculation of the porosity assumes that the transport numbers of Al\(^{3+}\) and O\(^{2-}\) ions in the film are 0.4 and 0.6, respectively, which is consistent with experimental values for barrier film formation [99]. The slopes were measured in the region immediately after the surge in voltage at the start of re-anodizing up to 410 V when dielectric breakdown commenced. The calculated values of the porosity apply to the inner 400 nm of the film thicknesses. The measurements were repeated twice, with the individual results differing by ≤ 1%. The results are given in Table 5-7.

Table 5-7. Porosities of films formed on aluminium for 1200 s at 22 V in 0.1 M H\(_2\)SO\(_4\) containing 0, 0.1, 0.5 and 1.0 wt.% fluorozirconic acid (FZ) at 0 and 20 °C.

<table>
<thead>
<tr>
<th>FZ wt.%</th>
<th>0</th>
<th>0.1</th>
<th>0.5</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>0° C</td>
<td>20° C</td>
<td>0° C</td>
<td>20° C</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>11.9</td>
<td>11.1</td>
<td>14.7</td>
<td>13.7</td>
</tr>
</tbody>
</table>

The porosities were not significantly affected by the temperature of the sulphuric acid electrolyte, but increased with additions of fluorozirconic acid, with values of 11.5%, 14.2%, 17.3% and 18.6% for 0, 0.1, 0.5 and 1.0 wt.% fluorozirconic acid.

5.2.7 Incorporation and distribution of fluorine

Porous films are formed by inward migration of O\(^{2-}\) ions in the barrier layer [96]. Outward migrating Al\(^{3+}\) ions are ejected at the pore bases to the electrolyte [116]. Only anion species are normally incorporated into the films from the electrolyte, e.g. sulphate [190, 222-224], phosphate [224, 225] or oxalate [226] ions from sulphuric, phosphoric and
oxalic acids. In the absence of film growth at the film/solution interface, located at the pore base, by outward migration of Al\(^{3+}\) ions, cation species, such as Zr\(^{4+}\) ions, originating from the electrolyte are not expected to be present in porous films.

The presence of fluorine and the absence of zirconium in the present films may be due to the following reactions:

\[
ZrF_6^{2-} + 2H_2O \rightarrow 2F^- + ZrO_2 + 4HF \\
\text{Or} \quad ZrF_6^{2-} \rightarrow ZrF_{n}^{(4-n)} + (6-n)F^-  \tag{5-2}
\]

The oxide species produced in (1) may dissolve in the electrolyte or Zr\(^{4+}\) may be ejected from the film surface under the influence of the electric field. HF may be released to the electrolyte and could attack the film or may provide a source of fluoride for incorporation into the film. Fluoride ions produced by progressive dissociation of fluorozirconic anions, according to (2), may be directly incorporated into the film or combine with H\(^+\) ions to form HF. The subsequently generated ZrF\(_3^+\) ions would migrate away from the film surface.

Alternatively, the following reactions may occur:

\[
ZrF_6^{2-} + H^+ \rightarrow ZrF_5^+ + HF \\
ZrF_5^- + 2H^+ + H_2O \rightarrow ZrOF^+ + 4HF  \tag{5-4}
\]

The charge on the ZrOF\(^+\) should also cause it to migrate from the oxide surface. An analogous species, TiOF\(^+\), is considered to be stable in solutions of titanium and fluoride ions [227].

The absence of zirconium species in the anodic films contrasts with the deposition of zirconium oxide during formation of conversion coatings on aluminium alloys. The latter is favoured at cathodic sites on the alloy surface where the pH is locally increased by reduction of oxygen, resulting in the reaction [228].

\[
ZrF_6^- + 4OH^- \rightarrow ZrO_2.2H_2O + 6 F^-  \tag{5-5}
\]
On the contrary, during anodizing, the anodic oxidation of the aluminium generates increased acidity according to the reaction:

$$2\text{Al} + 3 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^-$$  \hspace{1cm} 5-6

Thus, conditions for the deposition of zirconium oxide do not occur.

The similarity of the porosities of the films formed at 0 and 20 °C in electrolytes containing a particular concentration of fluorozirconic acid is unexpected from the results of dissolution of the barrier layer post anodizing, which show an increase by about a factor of ten in the rate of dissolution at 20 °C compared with 0 °C. This may be due to differences in the composition and temperature of the pore electrolyte during film growth. The generation of HF from fluorozirconate ions may also play a role in enhancing dissolution at 0 °C.

The results of the EDX analyses in Table 5-4 reveal that the F: Al ratios in films formed in electrolytes containing 3.5 x 10^{-2} and 3.5 x 10^{-1} M sodium fluoride are of a similar order as in films formed in the electrolytes containing 0.1 and 1.0 wt.% fluorozirconic acid, respectively. However, Table 5-1 shows that the concentrations of the fluoroacids are roughly an order of magnitude lower than the concentrations of the sodium fluoride and two orders of magnitude lower than the concentrations of free fluoride ions. This suggests that fluoride ions generated from fluorozirconate ions in reactions (5-1), (5-3) and (5-4) are the main source of fluoride ions in the film. Such a suggestion is consistent with the observation made in earlier published work that the addition of hexasilicate ions to oxalic acid has a greater influence on film growth than additions of fluoride ions [13].

A previous study of fluoride incorporation into barrier-type films showed that fluoride ions migrate inwards in anodic alumina at about twice the rate of O^{2-} ions [229]. Consequently, a fluoride-rich layer should be present next to the substrate and also along the cell boundaries in the present films, as illustrated in the schematic diagram of Figure 5-9.
The presence of a fluoride-rich layer was found by XPS analysis of a film formed in oxalic acid with added fluoride [14] and is suggested to be present in the films formed in sulphuric acid according to the GDOES profiles of Figure 5-6. The cells in the present films probably comprise three regions of different composition: a fluoride-rich region at the cell boundary, an intermediate region consisting of oxide and fluoride, formed since sulphate ions migrate inward more slowly than O\(^{2-}\) and fluoride ions, and a region next to the pore/electrolyte interface containing an oxide, fluoride and sulphate. A similar cell structure occurs in porous films formed on titanium [230, 231] and zirconium [18], where fluoride ions also migrate faster than O\(^{2-}\) ions.

The fluoride ions cause an increase in the growth rate of the film. However, the effect decreases with time due to the reduction in the rate of diffusion of fluoroacid anions and fluoride ions to the pore bases, and hence in the concentration of fluoride ions incorporated into the films. According to the EDX analyses of Table 5-4, the concentrations of fluoride ions in the films formed for 300 s in the presence of a fluoroacid at both 0 and 20 °C were similar to, or significantly greater than, the concentration of sulphate ions in the films. Furthermore, comparison with the control specimens showed that the incorporation of fluoride did not significantly influence the incorporation of sulphate. The same applied also to films formed in the presence of sodium fluoride at concentrations of 3.5 x 10\(^{-2}\) M and 3.5 x 10\(^{1}\) M. This behaviour contrasts with observations made for barrier type films.
formed in a range of mixed electrolytes [232]. For example, the incorporation of molybdenum species from a molybdate-tungstate electrolyte reduces the incorporation of tungsten species.

From the present results, it is not possible to identify the role of the fluorine species in enhancing the rate of film growth, and more than one mechanism may be operative. The authors have previously proposed that the pores in films formed in sulphuric acid at 20 °C, at current densities above about 2 mA cm\(^{-2}\) develop by the flow of oxide from the barrier layer into the cell walls [143]. Thus, the increased film growth rate is possibly due to an enhancement in the flow of the film material of the barrier layer due to the incorporation of aluminium fluoride units into the film. These species may alter the bonding within the anodic alumina and decrease the viscosity of the oxide. The flow may also be assisted by higher compressive stresses within the barrier layer due to the volume per mole of aluminium AlF\(_3\) being greater than that of Al\(_2\)O\(_3\) by a factor of about 1.6. The continuous etching of the barrier layer during film growth by HF generated at the base of the pores may be a further factor in the enhancement of the current density. From the average rates of film growth, determined from film thicknesses in Table 5-2, and the chemical dissolution rates of the films in Table 5-6, the ratios of the film dissolution rate to growth rates are calculated to be 0.5 x 10\(^{-3}\) and 1.2 x 10\(^{-3}\) for anodizing in the electrolyte containing 0.1 wt.% fluoroacid at 0 and 20 °C, respectively, and 1.5 x 10\(^{-3}\) and 9.5 x 10\(^{-3}\) for anodizing in the electrolyte containing 1 wt.% fluoroacid at 0 and 20 °C, respectively. However, the dissolution rates may be accelerated during film growth by the electric field and Joule heating and by an enhanced concentration of fluoride ions generated from the fluoroacid in reactions (5-1), (5-3) or (5-4). Thus, the significance of dissolution to the film growth is uncertain from the present results.

### 5.3 Conclusions

1. Additions of fluoroacid or sodium fluoride to sulphuric acid increase the growth rate of anodic films formed on aluminium under a constant voltage of 22 V at 0 and 20 °C. The effect of the fluoroacid addition on the increment in film thickness is greater at 0 °C than at 20 °C.

2. The growth rates of the films decrease with time of anodizing since diffusion controls the supply of fluoroacid anions and fluoride ions to the base of pores.
3. Increasing the concentration of the fluoroacid or sodium fluoride increases the growth rate. However, film dissolution is also enhanced. This can lead to the collapse of the porous structure at the film surface, which is promoted by increased fluoroacid/fluoride concentration and electrolyte temperature.

4. The films contain oxide, sulphate and fluoride species. Zirconium species are not incorporated into the films formed in electrolytes containing fluorozirconic acid. The incorporation of fluoride ions has negligible influence on the concentration of incorporated sulphate ions.

5. The migration rate of fluoride ions is faster than that of sulphate and oxide ions. Hence, it is expected that a fluoride-rich layer is present at the base of the barrier layer and at the cell boundaries.
6 Effect of fluorozirconic acid on anodizing of aluminium and AA 2024-T3 alloy in sulphuric and tartaric-sulphuric acids

6.1 Introduction

Sulphuric acid anodizing (SAA) is commonly used in industry for the protection of aluminium alloys against corrosion and wear [1, 46, 221, 222, 233]. Boric-sulphuric [8, 173, 234-236] and tartaric-sulphuric (TSA) [174, 175, 237-239] mixed acid anodizing processes have also been developed as alternatives to chromic acid anodizing for aircraft applications. Following anodizing, sealing treatments may be applied to enhance the corrosion resistance [240, 241]. The films may be formed at a range of temperatures, depending on the process and the application. Hard anodic films for wear resistance are usually produced at low electrolyte temperature and relatively high voltage to minimize chemical dissolution [242-244]. In contrast, TSA is generally carried out at an elevated temperature of about 37 °C [174, 175, 237-239].

The films formed by SAA and TSA processes are composed of amorphous alumina with incorporated sulphate or sulphide ions [46, 143, 174, 222, 223]. The film structure depends on the substrate composition and the anodizing conditions, ranging from linear porosity, typical of pure aluminium [8, 46, 143, 245], to a sponge-like porosity on copper-containing alloys [174, 246]. The films on commercial alloys usually contain a variety of defects such as voids or regions of altered structure and composition due to the local influences on film growth of intermetallic particles [247, 248]. Additionally, a significant fraction of the anodizing current may be consumed by the formation of oxygen gas [249], which can be evolved from a film formed both above the matrix [174] and intermetallic particles [162]. The oxygen can be formed within the alumina due to the reaction \( 2O^2- \rightarrow O_2 + 4e^- \), which occurs when the composition is modified by incorporated alloying elements, most notably copper, and results in bubbles of high-pressure oxygen gas [77]. Studies have shown that about 20 to 30% of the applied current is used in forming oxygen during anodizing AA 2024-T3 alloy in sulphuric acid [174, 249].

In a previous work [250], it was shown that addition of fluorozirconic acid (FZ) to sulphuric acid resulted in the incorporation of fluoride ions into the film and an enhancement in the oxidation rate of the aluminium that decreased with the time of anodizing. Ammonium hexafluorosilicate [13] and ammonium fluoride [13, 14] additions
to oxalic acid have also been shown to reduce the voltage during anodizing of aluminium under a constant current [13]. It was suggested that Si-F bonds may be broken under the high electric field to generate free fluoride ions, with incorporated fluoride ions subsequently migrating to the aluminium/film interface, where a fluoride-rich layer was identified [14]. It was proposed that the incorporated fluoride generates a space charge that promotes the injection of Al$^{3+}$ ions into the film thereby enhancing the current density [14]. Porous anodic films have also been formed in fluoroboric acid solutions [12]. The pore size was found to depend on the concentration and temperature of the solution and the time of anodizing. Details of the film composition were not provided.

The previous studies of the effects of fluorine species on anodizing have focused on aluminium. In the present study, the effect of FZ on anodizing of AA 2024-T3 alloy is investigated for SAA and TSA processes using a range of anodizing voltages and electrolyte temperatures.

### 6.2 Results and Discussion

#### 6.2.1 Anodizing AA 2024-T3 alloy at a constant voltage in sulphuric acid electrolytes containing 0, 0.1 and 0.5 wt.% fluorozirconic acid

Figure 6-1 (a) and (b) presents the current density-time curves for the AA 2024-T3 alloy anodized at 22 V for 1200 s, in 0.1 M and 1.0 M sulphuric acid containing 0, 0.1 and 0.5 wt.% FZ (Table 6-1) at 0 and 20 °C. The insets show the current density in the first 200 s. A high current density occurred immediately after the application of the voltage due to the high electric field across the initial oxide film on the alloy surface. The current density rapidly reduced as the film thickened and embryo pores were formed. Subsequently, a relatively constant current density was soon reached for the control specimens, associated with the steady growth of a porous film. In contrast, anodizing in the presence of FZ led to a minimum and subsequent peak current density after the initial current surge. Thereafter, the current density gradually decreased, in some instances approaching a steady value. In other cases, the current density decreased until the termination of anodizing, most noticeably with 0.5 wt.% FZ at 20 °C. In general, the current density was increased by the presence of FZ and increase in the temperature.
Figure 6-1. Current-density-time curves for AA2024-T3 alloy anodized at 22 V at 0 °C and 20 °C in (a) 0.1 M H₂SO₄ and (b) in 1 M H₂SO₄. Curves A and D – control specimens anodized without fluorozirconic acid; curves B and E – 0.1 wt.% fluorozirconic acid; curves C and F – 0.5 wt.% fluorozirconic acid, at 0 and 20 °C, respectively.

Figure 6-2 show scanning electron micrographs of the surface and cross-sections of films formed on the alloy at 0 °C in electrolytes containing 0, 0.1 and 0.5 wt.% FZ. The control specimen revealed a porous surface, with residues of oxidized second phase (see arrows).
Figure 6-2. Scanning electron micrographs (secondary electrons) of the surfaces (1st column) and cross-section (2nd column) of anodic films formed by anodizing AA 2024 alloy in 0.1 M sulphuric acid at 22 V at 0 °C for 1200 s; A – control; B - with 0.1% fluorozirconic acid and C- with 0.5% fluorozirconic acid.

Table 6-1. Concentrations of fluorozirconic acid (FZ), total fluorine and free fluoride added to 0.1 M sulphuric acid electrolyte.

<table>
<thead>
<tr>
<th>FZ addition to 0.1 M H₂SO₄</th>
<th>FZ concentration</th>
<th>Total fluorine concentration</th>
<th>Free fluoride</th>
</tr>
</thead>
<tbody>
<tr>
<td>(wt. %)</td>
<td>mol. dm⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>2.24 x 10⁻¹</td>
<td>1.34 x 10⁻²</td>
<td>3.46 x 10⁻⁴</td>
</tr>
<tr>
<td>0.5</td>
<td>1.12 x 10⁻²</td>
<td>6.72 x 10⁻²</td>
<td>1.73 x 10⁻⁴</td>
</tr>
<tr>
<td>1.0</td>
<td>2.24 x 10⁻²</td>
<td>1.34 x 10⁻¹</td>
<td>3.46 x 10⁻⁷</td>
</tr>
</tbody>
</table>
Table 6-2. Thicknesses of films, determined by SEM, and charge density passed for anodizing of AA 2024-T3 alloy for 1200 s at 22 V in 0.1 and 1.0 M H₂SO₄, without (control) and with the addition of 0.1 wt.% fluorozirconic acid at 0 and 20 °C.

<table>
<thead>
<tr>
<th>Sulphuric acid concentration</th>
<th>Control</th>
<th>0.1 % FZ</th>
<th>0.5 % FZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 M</td>
<td>1.0 M</td>
<td>0.1 M</td>
</tr>
<tr>
<td>0 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film thickness (µm)</td>
<td>0.16 ± 0.01</td>
<td>0.55 ± 0.01</td>
<td>0.49 ± 0.02</td>
</tr>
<tr>
<td>Charge density (C/cm²)</td>
<td>0.881</td>
<td>2.226</td>
<td>1.806</td>
</tr>
<tr>
<td>Ratio (µm cm²/mC)</td>
<td>0.19</td>
<td>0.25</td>
<td>0.27</td>
</tr>
<tr>
<td>20 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film thickness (µm)</td>
<td>0.57 ± 0.03</td>
<td>n.d.</td>
<td>1.25 ± 0.07</td>
</tr>
<tr>
<td>Charge density (C/cm²)</td>
<td>2.548</td>
<td>n.d.</td>
<td>5.018</td>
</tr>
<tr>
<td>Ratio (µm cm²/mC)</td>
<td>0.22</td>
<td>n.d.</td>
<td>0.25</td>
</tr>
</tbody>
</table>

In contrast, the localized disintegration of the cellular film structure was evident with 0.1 wt.% FZ due to the increased chemical dissolution of the film. With the increase of the concentration of FZ to 0.5 wt%, further disintegration of the cellular structure occurred, which generated a relative coarse porosity. The cross-section indicated that the severe chemical dissolution affected the outer 70% of the film thickness. Due to the increasing fragility of the degraded film, some material may have been dislodged during sectioning. The film cross-sections revealed a layer-like structure in regions unaffected by severe chemical dissolution under all of the selected anodizing conditions of Table 6-2. A similar morphology has been reported previously for films formed on model Al-Cu alloys and AA 2024-T3 alloy in sulphuric acid and sulphuric-tartaric acid [174].

Table 6-2 presents the film thicknesses, the charge densities passed in forming the films and the thickness: charge density ratios. Following anodizing of the alloy at 0°C in 0.1 M sulphuric acid, the film thickness was increased by factors of about 3.1 and 8.8 relative to the control specimen by additions of 0.1 and 0.5 wt.% FZ, respectively, and by factors of about 2.2 and 1.3 at 20 °C. The film thickness: charge density ratios were in the range 0.07 to 0.29. These ratios compare with a ratio of about 0.45 for anodizing relatively pure aluminium under similar conditions [250]. During anodizing of aluminium, oxidation of aluminium is the primary electrochemical reaction, and generation of oxygen is negligible.
Hence, a film thickness : charge density ratio of 0.45 μm cm$^{-2}$ C$^{-1}$, is equivalent to an expansion factor (thickness of film : thickness of oxidized aluminium) of about 1.30. Expansion factors close to this value have been reported in the literature, with data showing an increase in the expansion factor with an increase of the anodizing voltage or the current density and a decrease with the increase of the temperature [143, 144, 253]. Following anodizing in 1.0 M sulphuric acid at 0 °C, the film thickness was increased by factors of about 2.3 and 4.8 by additions of 0.1 and 0.5 wt.% FZ respectively. Cell collapse at the film surface occurred with 0.5 wt.% FZ at 0 °C and also with 0.1 and 0.5 wt.% FZ at 20 °C. Chemical dissolution was negligible at 0 °C in the presence of 0.1 wt.% FZ, resulting in a thickness : charge density ratio of 0.32 μm cm$^{-2}$ C$^{-1}$.

The low thickness : charge density ratios for the alloy compared with aluminium result mainly from oxygen evolution during anodizing. However, chemical dissolution also contributed significantly to a low film thickness in the presence of 0.5 wt.% FZ in 0.1 M sulphuric acid at 20 °C and in 1.0 M sulphuric acid at 0 °C. The relatively low ratio of 0.19 μm cm$^{-2}$ C$^{-1}$ for the control specimens at 0 °C may be due to the presence of intermetallic particles on the etched alloy surface, which enhance oxygen evolution in the early stages of anodizing. The particles are oxidized preferentially to the matrix at voltages of about 0 V$_{SCE}$ for Al-Cu-Mg particles and 5 - 6 V$_{SCE}$ for Al-Cu particles [246].

EDX analyses were made at the surface of films formed at 22 V for 1200 s, in 1 M sulphuric acid at 0 °C with the addition of 0.1 and 0.5 wt.% FZ. The analyses were carried out at an accelerating voltage of 5 to 7 kV in a square of the area of dimensions 10 x 10 μm. 1.4 and 2.6 at.% fluorine were detected in the respective films, with F:Al atomic ratios of 0.04 and 0.08. The former concentration is similar to that in films formed at 22 V for 300 s on aluminium in a similar electrolyte [250]. The sulphur concentration was about 2.8 at.%, with an S:Al ratio of 0.10 for films formed in the presence of both 0.1 and 0.5 wt.% FZ.

Analyses were also made using an accelerating voltage of 5 kV in three rectangular areas, of size 3.0 x 0.3 μm, in a cross-section of a film formed in the presence of 0.1 wt.% FZ. The fluorine concentration was 1.2, 1.3 and 1.0 at.% in the outer, middle and inner regions of the film. Zirconium was not detected, which is consistent with previous findings for aluminium anodized in the presence of FZ. It has been suggested that the absence of
zirconium may be due to the following reactions of fluorozirconate ions adsorbed at the pore bases [250], which occur under the influence of a high electric field:

\[
\text{ZrF}_6^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{F}^- + \text{ZrO}_2 + 4\text{HF}
\]

or

\[
\text{ZrF}_6^{2-} \rightarrow \text{ZrF}_{n}^{(4-n)} + (6-n)\text{F}^-
\]

Any zirconium species formed by reaction (6-1) would not be expected to be incorporated into porous alumina films since Zr\textsuperscript{4+} ions migrate outward in the anodic alumina at a similar rate as Al\textsuperscript{3+} ions [254] and may be ejected to the electrolyte at the pore bases. Reaction (6-2) would progressively strip fluoride ions from fluorozirconate ions, generating ZrF\textsubscript{3}\textsuperscript{+} that would migrate away from the pore bases. Released fluoride ions and fluoride from HF would probably be incorporated into the film.

The Cu:Al ratio was \( \approx 0, 3 \times 10^{-4} \) and 0.003 in the outer, middle and inner regions of the film, respectively, compared with 0.019 in the alloy. The last of these ratios is 16\% of that in the alloy, which indicates a large loss of copper species during anodizing.

### 6.2.2 Anodizing of aluminium and AA 2024.T3 alloy in tartaric-sulphuric acid electrolytes containing 0, 0.1 and 0.5 wt.% fluorozirconic acid

The current density during stepped voltage anodizing to 14 V of aluminium and AA 2024-T3 alloy in TSA, without and with the addition of 0.1 wt.% FZ at 0, 20 and 37 °C, are shown in Figure 6-3 (a) and 6-3 (b), respectively. The total anodizing time was 1560 s. Each voltage step caused a current surge due to the increased electric field, followed by a reduction in the current as the barrier layer thickened. After the final voltage step, a steady current was soon reached for the FZ-free electrolyte, which was maintained until the termination of anodizing. In contrast, in the presence of 0.1 wt.% FZ, the current gradually decreased until anodizing was stopped. The current density increased significantly with the increase of the temperature. The FZ had a greater influence on the current density during the early stages of the anodizing period than at later times. The final current density for aluminium at 0 °C was increased by FZ by about 150 \%. However, at 20 and 37 °C, the increase was comparatively negligible. For the alloy, the greatest increase in the final current density also occurred at 0 °C (200\%) with a smaller enhancement at 20 °C (41\%), and a negligible enhancement at 37 °C. The final current densities for the alloy were either similar to, or lower than, those of the aluminium.
The aluminium and alloy were also anodized to 18 V (Figure 6-4 (a) and 6-4 (b), respectively). The use of both 14 and 18 V for anodizing was made, since, as later explained, the anodizing voltage affected the ratio of the film growth rate on the alloy relative to aluminium and the enhancement by FZ of the rate of film growth relative to the control specimens, the latter particularly at 0 °C. Similarly to 14V, the final current density was enhanced significantly only at 0 °C for aluminium, and at 20 and 0 °C for the alloy when the enhancements were similar, about 50%.

The effect of FZ at longer times was determined by anodizing at a constant voltage of 18 V for 7200 s at 0 and 20 °C. Anodizing at 37 °C was not carried out since the previous results showed no benefit of FZ at this temperature. The current density-time curves for aluminium and the alloy (Figure 6-5 (a) and 6-5 (b), respectively) at both temperatures showed an increased current density due to FZ that persisted until the termination of anodizing.
Figure 6-3. Current-density-time curves for (a) aluminium and (b) AA 2024 alloy anodized to 14 V in 0.53 M tartaric/0.4 M sulphuric acid without and with 0.1 wt.% fluorozirconic acid. Curves A, B and C – control specimens anodized without fluorozirconic acid; curves D, E and F – 0.1 wt.% fluorozirconic acid, at 0, 20 and 37 °C, respectively.
Figure 6-4. Current-density-time curves for (a) aluminium and (b) AA 2024 alloy anodized to 18 V in 0.53 M tartaric /0.4 M sulphuric acid without and with 0.1 wt.% fluorozirconic acid. Curves A, B and C – control specimens anodized without fluorozirconic acid; curves D, E and F – 0.1 wt.% fluorozirconic acid, at 0, 20 and 37 °C, respectively.
Figure 6-5. Current-density-time curves for (a) aluminium and (b) AA 2024 alloy anodized at 18 V in 0.4 M sulphuric/0.53 tartaric acid without and with 0.1 wt.% fluorozirconic acid. Curves A and B – control specimens anodized without fluorozirconic acid; curves C and D – 0.1 wt.% fluorozirconic acid, at 0 and 20 °C, respectively.

Figure 6-6 presents scanning electron micrographs of the surfaces of films formed on aluminium (curves A-F) and AA 2024-T3 alloy (curves G-L), respectively, anodized to 18
V at 0, 20 and 37 °C, for a total time of 1560 s. An integral porous structure is evident at all temperatures for the aluminium. A network of ridges is present that forms in the early stage of anodizing, coinciding with ridges on the electropolished aluminium surface [255]. The network was only faintly evident in the film formed on aluminium at 37 °C in the presence of FZ, indicating a slight loss of material due to chemical dissolution.

A ridge network was also observable in films on the alloy in the absence of FZ at all temperatures and in the presence of FZ at 0 °C. The network was not observable at 20 °C, although the film did not appear significantly degraded. In contrast, at 37 °C, the cellular structure was severely degraded. The film formed at 20 °C in the presence of FZ was less degraded than the film formed for 1200 s at 22 V in 0.1 M sulphuric acid containing a similar amount of FZ (Figure 7-4 G), despite a higher acid concentration. The reduced degradation is possibly due to the presence of the tartaric acid, which has been shown to lower the rate of chemical dissolution [10].
Table 6-3 list the film thicknesses and the thickness : charge density ratios for the aluminium and AA 2024-T3 alloy, respectively, anodized using voltage steps to 14 and 18 V, with an anodizing time of 1560 s, and also using a constant 18 V, with an anodizing time of 7200 s. Specimens anodized in the FZ-free electrolyte and in the presence of 0.1 wt.% FZ were compared. The film thickness: charge density ratio for aluminium specimens ranged from 0.41 to 0.50 μm cm$^2$ C$^{-1}$, apart from the specimen anodized at 18 V for 7200 s at 20 °C that had a lower ratio of 0.31 μm cm$^2$ C$^{-1}$ due to the collapse of the cell structure caused by chemical dissolution. In contrast, the ratios for the alloy, excluding films which revealed cell collapse, ranged from 0.20 to 0.32 μm cm$^2$ C$^{-1}$. The individual ratios within the ranges did not depend significantly on the electrolyte temperature, the anodizing voltage or the electrolyte composition. The lower ratios for the alloy are due mainly to oxygen evolution that accompanies film growth. Loss of film thickness due to chemical dissolution was restricted to aluminium and the alloy specimens anodized for 7200 s at 20 and 37 °C in the presence of FZ. Following anodizing at 0 °C, the films formed in the presence of FZ were thicker than the control films, irrespective of the anodizing voltage and the anodizing time, by an average factor of 2.3. The difference in thickness was reduced at 20 °C, with some anodizing conditions resulting in negligible difference. The average factor was 1.2. At 37 °C, the FZ led to no significant increase in film thickness.

For both aluminium and the AA 2024-T3 alloy stepped voltage anodized at 18 V, the film thickness measured from cross-sections observed by SEM increased with the electrolyte temperature. The FZ increased the film thickness by a factor of about 2.0 at 0 °C, compared with a factor of about 2.8 for anodizing at 14 V. However, the effect of the FZ decreased with temperature and was negligible at 37 °C. If the anodizing time was extended to 7200 s under a constant voltage of 18 V, chemical dissolution in the presence of FZ reduced the film thickness significantly at 20 °C, with the thickness: charge density ratio decreasing to 0.31 for aluminium and to 0.19 for the alloy. In contrast, at 0 °C, chemical dissolution was insignificant.

Figure 6-7 (a) and 6-7 (b) shows the dependence of the film growth rates on the electrolyte temperature for the aluminium and AA 2024-T3 alloy, respectively, anodized to 18 V for 1560 s. The results reveal a linear dependence on the logarithm of the growth rate on the inverse temperature, consistent with film growth controlled by field-assisted ionic
migration. The growth rates for aluminium were greater than for the alloy, by a factor of 2.0, at all temperatures in the FZ-free electrolyte, and by factors of 2.2, 1.6 and 2.0 times at 0, 20 and 37 °C, respectively, in the electrolyte containing 0.1 wt.% FZ. In comparison, films grown for 1560 s with stepping of the voltage to 14 V revealed faster growth on aluminium by factors of 1.3, 1.4 and 1.5 in FZ-free electrolyte at 0, 20 and 37 °C, respectively, and by factors of 1.2, 1.1 and 1.5 in the electrolyte containing 0.1 wt.% FZ. Thus, the lower voltage resulted in a smaller difference between the growth rates on the aluminium and the alloy. The difference in rates reduced from about 2.0 at 18 V to 1.4 at 14 V.

EDX analyses were made on films formed for 600 s at a constant voltage of 18 V on the AA 2024-T3 alloy in TSA with the addition of 0.1 wt.% FZ. The anodizing time was selected to avoid significant film dissolution that might affect the fluorine content of the outer regions of films formed for longer times. The EDX analyses were carried out at the film surface in a square of area 10 x 10 μm. The accelerating voltage in the range 5 to 10 kV was chosen to avoid detection of X-rays from the alloy. In confirmation, the O:Al ratio was in the range 1.57 to 1.63, which are reasonable values for anodic alumina containing incorporated sulphate ions. Carbon, which could originate for tartaric acid species in the film, was disregarded from the analyses since the small carbon peaks were of similar magnitude to those obtained from the presence of carbon contamination of films formed using sulphuric acid alone. The EDX results revealed atomic ratios of F:Al of 0.05, 0.03 and 0.02 for the films formed at 0, 20 and 37 °C, respectively, with fluorine concentrations of 1.6, 1.2 and 0.7 at.%. The S:Al ratios in the films were about 0.08, with a sulphur concentration of about 2.8 at.%, which was also found in analyses of the control specimens formed in the FZ-free electrolyte at the respective temperatures.

In an earlier study, the F:Al ratio in films formed for 300 s on aluminium at 22 V in 0.1 M sulphuric acid containing 0.1 wt.% FZ at 0 and 20 °C were determined to be 0.06 and 0.07, respectively [250]. The ratios reduced to 0.03 and 0.02 when the acid concentration was increased to 1.0 M. The F:Al ratios determined for the films formed in TSA at 0 and 20 °C are compatible with the earlier values, given the different concentration of the sulphuric acid in TSA and the presence of tartaric acid.
In order to determine whether an increased FZ concentration would increase the current density at 0, 20 and 37 °C, stepped voltage anodizing to 14 V was carried out of aluminium for 1560 s in TSA containing 0.5 wt.% FZ. The current density-time curves are shown in Figure 6-8. The charge densities passed were 4.841, 9.850 and 18.805 cm² C⁻¹ at the respective temperatures, which represented increases in the charge density by factors of 3.02, 2.93 and 2.10 compared with anodizing in the presence of 0.1 wt.% FZ and 7.70, 3.76 and 2.28 with respect to the control specimens. Figure 6-9 displays cross-sections of the films, which are compared with the films formed on specimens anodized in the absence of FZ and in the presence of 0.1 wt.% FZ. The thicknesses of the control films, given in Table 3, increased by factors of about 2.73, 1.22 and 1.06 due to the presence of 0.1 wt.% FZ at 0, 20 and 37 °C, respectively. The thickness of the films formed in 0.5 wt.% FZ were 1.55, 2.37 and 2.67 μm at 0, 20 and 37 °C, respectively. Figure 6-10 presents the results of the thickness measurements graphically, with best fit straight lines shown. The thicknesses at 0 and 20 °C represent increases by a factor of about 5.96 and 1.91 with respect to the respective control specimens. However, at 37 °C, the thickness was reduced compared with the control specimen by a factor of about 0.68. The thickness : charge density ratios were about 0.32, 0.24 and 0.14 μm cm² C⁻¹ for anodizing at 0, 20 and 37 °C, respectively. In comparison, the ratios for the control specimens and for specimens anodized in the presence of 0.1 wt. % FZ were about 0.46 μm cm² C⁻¹. Thus, it can be estimated that about 30, 50 and 70 % of the film thickness has been lost due to chemical dissolution during anodizing in the presence of 0.5 wt.% FZ at 0, 20 and 37 °C, respectively.
Figure 6-7. Dependence of the growth rates of the films on (a) aluminium and (b) AA 2024-T3 alloy on temperature; ★ specimens anodized in TSA up to 14 V; ■ specimens anodized in TSA up to 18 V; ● specimens anodized in TSA with 0.1 % fluorozirconic acid up to 14 V; ▼ specimens anodized in TSA with 0.1 % fluorozirconic acid up to 18 V.
Figure 6-8. Current-density-time curves for aluminium anodized to 14 V in 0.53 M tartaric /0.4 M sulphuric acid without fluorozirconic acid, curves A, B and C, and with 0.5wt.% fluorozirconic acid, curves D, E and F, at 0, 20 and 37 °C.
Figure 6-9. Scanning electron micrographs (secondary electrons) of cross-sections of anodic films formed by anodizing aluminium to 14 V for 1560 s in 0.53 M tartaric / 0.4 M sulphuric acid; 1\textsuperscript{st} row anodized at 0 °C; 2\textsuperscript{nd} row anodized at 20 °C; 3\textsuperscript{rd} row anodized at 37 °C; A, B and C – control specimens; D, E and F - with 0.1% fluorozirconic acid and G, H and I- with 0.5% fluorozirconic acid.
Figure 6-10. Thickness of films formed on aluminium following anodizing at 14 V for 1560 s in 0.4 M sulphuric/0.53 tartaric acid with different FZ addition at ■ 0 °C, ● 20 °C, ▲ 37 °C.

EDX analyses made at the film surface of specimens stepped voltage anodized to 14 V for 1560 s in TSA containing 0.5 wt.% FZ at 20 and 37 °C. The films contained 5.0 and 3.3 at.% fluorine at the respective temperature, with F:Al ratios of 0.13 and 0.09. The S:Al ratios were similar in the two films, about 0.06, corresponding to about 2.0 at.% sulphur. Thus, by comparison with the previous analyses of the film formed in electrolyte containing 0.1 wt.% FZ, the incorporation of fluorine was significantly increased by increasing the FZ concentration in the electrolyte to 0.5 wt.%, while the S:Al was reduced from 0.08 to 0.06.

The irregular surface regions in the cross-sections of films formed at 20 and 37 °C clearly indicated that significant chemical dissolution had occurred during anodizing (Figure 6-9). The rate of dissolution was greater at 37 °C causing a large reduction in the film thickness. Less severe chemical dissolution at 0 and 20 °C enabled significant gains in the film thickness relative to the control conditions. Gains in film thickness could also be obtained at 20 °C using a shorter anodizing time with an increased concentration of FZ acid. A time of 780 s, which is 50% of the previous anodizing time, and 0.5 wt. % FZ led to a film that was thicker than the control film formed for 1560 s by a factor of about 1.7. However,
using a time of 520 s and 0.5 wt.% FZ for specimen anodized up to 14 V at 37 °C led to a reduction in the film thickness by a factor of about 0.48 compared with the control specimen anodized for 1560 s. Films of similar thickness, 2.1 μm at 20 °C and 1.9 μm at 37 °C were obtained, with cross-sections of both film revealing degradation due to chemical dissolution in the outer 10 to 20 % of the film thickness, resembling that shown in Figure 6-9 H. Similarly reduced anodized times for the AA 2024-T3 alloy resulted in films about 0.9 μm thick, similar to the thickness of the control film at 20 °C and about one-third of the thickness of the control film at 37 °C. Investigations of FZ acid concentrations between 0.1 and 0.5 wt.% FZ may identify more favourable anodizing conditions for generation of films similar in thickness to control films at 37 °C with a reduced anodizing time and chemical dissolution.
Table 6-3. Thicknesses of films, determined by SEM, the charge density passed and the ratio of the thickness to the charge for anodizing of aluminium and AA 2024-T3 alloy in 0.53 M tartaric /0.4 M sulphuric acid without (control) and with addition of 0.1 wt.% fluorozirconic acid, at 0, 20 and 37 °C. The anodizing was carried out by their stepping the voltage to 14 or 18 V, or under a constant voltage of 18 V.

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Stepped (14 V)</th>
<th>Stepped (18 V)</th>
<th>Const. 18 V</th>
<th>Stepped (14 V)</th>
<th>Stepped (18 V)</th>
<th>Const.18 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Control</td>
<td>0.1 % FZ</td>
<td>Control</td>
<td>0.1 % FZ</td>
<td>Control</td>
<td>0.1 % FZ</td>
</tr>
<tr>
<td>Anodizing time (s)</td>
<td>1560</td>
<td>7200</td>
<td>1560</td>
<td>7200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film thickness (µm)</td>
<td>0.26 ± 0.01</td>
<td>0.71 ± 0.01</td>
<td>0.46 ± 0.01</td>
<td>0.98 ± 0.01</td>
<td>2.39 ± 0.02</td>
<td>6.09 ± 0.03</td>
</tr>
<tr>
<td>Charge density (C/cm²)</td>
<td>629</td>
<td>1.605</td>
<td>1.104</td>
<td>2.288</td>
<td>5.426</td>
<td>12.289</td>
</tr>
<tr>
<td>Ratio (µm cm²/C)</td>
<td>0.41</td>
<td>0.44</td>
<td>0.41</td>
<td>0.43</td>
<td>0.44</td>
<td>0.50</td>
</tr>
<tr>
<td>20 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film thickness (µm)</td>
<td>1.24 ± 0.01</td>
<td>1.51 ± 0.01</td>
<td>2.27 ± 0.05</td>
<td>2.45 ± 0.01</td>
<td>11.40 ± 0.01</td>
<td><strong>10.9 ± 0.2</strong></td>
</tr>
<tr>
<td>Charge density (C/cm²)</td>
<td>2.618</td>
<td>3.359</td>
<td>4.871</td>
<td>5.159</td>
<td>24.260</td>
<td><strong>35.788</strong></td>
</tr>
<tr>
<td>Ratio (µm cm²/C)</td>
<td>0.47</td>
<td>0.45</td>
<td>0.47</td>
<td>0.48</td>
<td>0.47</td>
<td><strong>0.31</strong></td>
</tr>
<tr>
<td>37 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film thickness (µm)</td>
<td>3.90 ± 0.01</td>
<td>4.12 ± 0.02</td>
<td>6.69 ± 0.02</td>
<td>6.58 ± 0.01</td>
<td>2.66 ± 0.06</td>
<td>2.77 ± 0.03</td>
</tr>
<tr>
<td>Ratio (µm cm²/C)</td>
<td>0.47</td>
<td>0.46</td>
<td>0.46</td>
<td>0.44</td>
<td>0.30</td>
<td>0.30</td>
</tr>
</tbody>
</table>
6.2.3 Possible roles of fluoride ions in anodic film growth

In the present work, the main effects of the FZ additions to sulphuric acid or TSA were to incorporate fluoride ions into the films and to increase the current density during anodizing under voltage control. However, the current density enhancement due to the fluoride ions was significantly dependent on the electrolyte temperature and the FZ concentration. The effect of the fluoride ions decreased with increasing temperature from 0 to 37 °C and was negligible at 37 °C for an addition of 0.1 wt.% FZ. The diminishing effect of the fluoride ions correlated with a reducing fluoride concentration in the film. Using a higher concentration of 0.5 wt.% FZ in the electrolyte, the current density and also the fluoride concentration in the film could be enhanced at 37 °C, although the film thickness was reduced by relatively severe chemical dissolution. Fluoride ions might influence the film growth rate through one or more of a number of possible mechanisms, which are considered below. However, the actual operative mechanisms cannot be separated by the results of the present study.

The formation of porous anodic films on aluminium involves counter migration of \( \text{Al}^{3+} \) and \( \text{O}^{2-} \) ions in the barrier layer by a process that largely conserves the ionic order \([96, 116]\). The inward migration of \( \text{O}^{2-} \) ions results in the formation of new oxide at the aluminium/film interface, while outward migrating \( \text{Al}^{3+} \) ions are ejected to the electrolyte at the pore bases under the influence of the electric field \([116]\). Sulphate ions are also incorporated into films formed in sulphuric acid \([222]\). The films formed in TSA may additionally contain tartrate ions. Sulphate ions migrate inward in the barrier layer more slowly than \( \text{O}^{2-} \) ions and, hence, resulting in a thin sulphate-free layer at the film base and along the cell boundaries \([149]\).

Two main mechanisms have been proposed for the development of pores in porous films on aluminium. Originally, the focus was placed mainly on pore generation owing to the field-assisted dissolution of the oxide at the pore bases \([127]\). This was considered to occur at a rate that balanced the rate of formation of new oxide at the aluminium/film interface in order to maintain a constant thickness of the barrier. Such dissolution might be enhanced fluoride ions, with increased etching of the barrier layer leading to an increased current density. More, recently, it has been shown that pores can develop due to oxide flow from barrier layer toward the cell walls \([129]\). The flow maintains a constant barrier layer thickness without the need for field-assisted dissolution of the oxide. Oxide flow has been
demonstrated by the behaviour of tungsten nanolayers initially incorporated within sputtering-deposited aluminium. Following oxidation of the tungsten oxide flow transported W<sup>6+</sup> ions to the cell walls and prevented their migration to the pore bases [129]. Oxide flow has also been demonstrated in work [147, 256, 257], and the behaviour of tungsten tracers mathematically modelled [130]. The oxide flows in response to compressive stresses in the barrier layer, with the ionic transport process in the barrier layer, that involves the simultaneous migration of a large proportion of the constituent ions, enabling the oxide to deform plastically [217]. The fluoride ions might assist oxide flow by lowering the viscosity of the alumina.

The amount of fluoride in the present films increased with the increase of the concentration of FZ in the electrolyte. The fluoride concentration was lower than the sulphate concentration in films formed in electrolytes containing 0.1 wt.% FZ but could exceed the sulphate concentration in films formed in the presence of 0.5 wt.% FZ. Fluoride incorporation from electrolytes containing 0.1 wt.% FZ did not significantly affect the incorporation of sulphate ions since the films formed in the presence of FZ contained similar concentrations of sulphate as films formed in FZ-free sulphuric acid. The presence of 0.5 wt% FZ led to a reduction in the sulphate content by about 25%.

Incorporated anions, such a phosphate and sulphate, have been shown to give rise to compressive stress in anodic alumina films [258, 259]. The incorporated sulphate can contribute to the compressive stress in the barrier layer owing to the high value of the ratio of the volume per aluminium ion in Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> relative to the volume per metal atom in aluminium (≈6.40) (Pilling-Bedworth ratio (PBR) relative to that of Al<sub>2</sub>O<sub>3</sub> (≈1.65). The incorporation of units of AlF<sub>3</sub> (PBR ≈ 2.9) into the film additional to the sulphate ions may further increase the compressive stress in the barrier layer. It has also been found that incorporated anions may influence the electric field across the barrier layer through introduction of a permanent polarization of the film that remains after anodizing has been terminated, with a positive charge remaining in the metal and a negative charge, associated with the presence of the anions, at the film surface [260]. Fluoride within the film may also increase the ionic current through reducing the activation energy or increasing the activation dipole for ionic transport under a particular value of the electric field [181]. The fluoride ions migrate through the barrier layer faster than O<sup>2-</sup> ions. A difference in their migration rates of about a factor of two has been determined for migration through a
barrier type film [229]. As a consequence of the faster migration of fluoride ions, a fluoride-rich layer is formed at the base of the film, with a thickness of a few nanometres. A thin fluoride-rich layer has also been detected by X-ray photoelectron spectroscopy at the base of porous films formed on high purity aluminium in oxalic acid [250]. During porous film growth, the fluoride ions initially located in the fluoride-rich layer at the base of the barrier layer are expected to be incorporated into the cell walls, forming a thin fluoride-rich region at the cell boundaries. This would be consistent with observations of other types of porous anodic film in which fluoride ions migrate faster than $O^{2-}$ ions, for example, porous films formed on titanium and zirconium in fluoride-containing electrolytes [18, 231].

### 6.3 Conclusions

1. The addition of FZ to sulphuric acid or TSA increases the rate of film growth during anodizing of aluminium and AA 2024-T3 alloy, with the effect reducing with an increase in anodizing time, temperature and concentration of the sulphuric acid. The increased growth rate may be offset by increased chemical dissolution, leading to collapse of the cell structure and film thinning, especially at a higher temperature and sulphuric acid concentration.

2. The presence of 0.1 wt.% FZ in TSA increases the rate of film growth on the AA 2024-T3 alloy by a factor of about 2.3 during anodizing at 14 or 18 V at 0 °C for times up to 7200 s. The factor reduces to roughly 1.2 at 20 °C. No significant thickness enhancement occurs at 37 °C.

3. Although FZ enhances the rate of chemical dissolution of the film, no loss of film thickness occurred for films formed on aluminium and the AA 2024-T3 alloy for times up to 7200 s in electrolytes containing 0.1 wt.% FZ at 0 °C, or for films formed for 1560 s at 20 and 37 °C. Anodizing for 7200 s at 20 and 37 °C led to the collapse of the cell structure due to pore wall thinning.

4. Increasing the FZ concentration to 0.5 wt.%, further increased the growth rate on aluminium relative to control specimens, by factors of about 6.0 and 1.9 at 0 and 20 °C respectively, but increased chemical dissolution reduced the film thickness at 37 °C.
5. Fluoride and sulphate ions are incorporated into the anodic alumina. The concentration of the fluoride ions in the film decreases with increasing temperature. However, the concentration of sulphate ions is not significantly affected. Zirconium-containing species are negligible constituents of the films.
7 Effect of fluoroacid type on anodizing of aluminium and AA 2024 –T3 alloy

7.1 Introduction

In the present study, the addition of sodium fluoride to the electrolyte was used to investigate the effect of free fluoride ions on the growth of barrier-type films on aluminium [229]. The effect of free and bonded fluoride ions on anodic film growth was investigated by constant voltage anodizing of aluminium in sulphuric acid with fluorozirconic acid addition. The study revealed that the addition of fluorozirconic acid increases the anodic film growth rate, with a dependence on the fluoroacid concentration, the electrolyte temperature and the anodizing time [250]. Other investigations were carried out to determine the effect of fluorozirconic acid on anodic film growth rate and film composition on AA 2024-T3 alloy [261].

Herein, the effects of different bonded fluoride species on the anodic film growth rate and composition were examined by scanning electron microscopy, EDX analysis, and GDOES. Specifically, the influences of fluoroboric, fluorosilicic, fluorotitanic and fluorozirconic acids are compared.

7.2 Results and Discussion

7.2.1 Current density-time curves and film morphologies

Anodizing of aluminium and AA 2024-T3 alloy specimens in 0.1 M sulphuric acid with addition of fluoroacids for 1200 s at a constant voltage of 22 V alters the current density-time response curves in comparison with anodizing in the fluoroacid-free electrolyte. The curve profiles showed similar trends for the different types of fluoroacids. Figure 7-1 (a, b, c and d) for aluminium and Figure 7-2 (a, b, c and d) for AA 2024-T3 alloy, shows the effect on the current density from the addition of 0.1 wt.% fluoroacids at 0 °C, 0.1wt.% fluoroacids at 20 °C, 0.5wt.% fluoroacids at 0 °C and 0.5wt.% fluoroacids at 20 °C, respectively. The molar concentrations of the fluoroacids and free-fluoride ions added to the electrolytes are given in Table 7-1.

The curve profiles showed similar trends for the different types of fluoroacids. A peak current density occurred for all specimens immediately on the application of the voltage due to the rapid growth of a barrier layer under a very high initial electric field.
The current density then rapidly decreased to a minimum value due to the reduction in the field as the film thickened. Around the minimum current density, embryo pores develop. A second current density peak occurred shortly after the start of anodizing, followed by a slow decline towards a steady value. The second peak and decline were absent for specimens formed in the fluoroacid-free electrolyte. Additions of 0.1 wt.% of fluoroacids caused an increment in the current density-time response curves. The increments depended on the fluoroacid type, concentration and anodizing condition.

Figure 7-1. Current-density-time curves for aluminium anodized at 22 V in 0.1 M H₂SO₄ at 0 °C (figures a and c) and 20 °C (figures b and d); A and F – control specimen; B and I - 0.1% fluorozirconic acid; K and O - 0.5% fluorozirconic acid; C and H - 0.1% fluorosilicic acid; L and P - 0.5% fluorosilicic acid; D and J - 0.1% fluorotitanic acid; M and Q - 0.5% fluorotitanic acid; E and G - 0.1% fluoroboric acid and N and R - 0.5% fluoroboric acid.
Figure 7-2 Current-density-time curves for AA 2024-T3 alloy anodized at 22 V in 0.1 M H$_2$SO$_4$ at 0 °C (figures a and c) and 20 °C (figures b and d); A and F – control specimen; B and I - 0.1% fluorozirconic acid; K and O - 0.5% fluorozirconic acid; C and H - 0.1% fluoroosilicic acid; L and P - 0.5% fluoroosilicic acid; D and J - 0.1% fluorotitanic acid; M and Q - 0.5% fluorotitanic acid; E and G - 0.1% fluoroboric acid and N and R - 0.5% fluoroboric acid.

Table 7-1. Concentrations of fluoroacid and free fluoride added to 0.1 M sulphuric acid electrolytes.

<table>
<thead>
<tr>
<th>Fluoroacid addition to 0.1 M H$_2$SO$_4$</th>
<th>Fluoroacid concentration in 0.1 M H$_2$SO$_4$</th>
<th>Total fluorine concentration in 0.1 M H$_2$SO$_4$</th>
<th>Free fluoride added to 0.1 M H$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1% H$_2$BF$_4$ (50%)</td>
<td>5.75 x 10$^{-3}$</td>
<td>2.30 x 10$^{-2}$</td>
<td>4.59 x 10$^{-4}$</td>
</tr>
<tr>
<td>0.1% H$_2$SiF$_6$ (35%)</td>
<td>2.45 x 10$^{-3}$</td>
<td>1.47 x 10$^{-2}$</td>
<td>2.01 x 10$^{-4}$</td>
</tr>
<tr>
<td>0.1% H$_2$TiF$_6$ (52%)</td>
<td>3.19 x 10$^{-3}$</td>
<td>1.91 x 10$^{-2}$</td>
<td>7.86 x 10$^{-4}$</td>
</tr>
<tr>
<td>0.1% H$_2$ZrF$_6$ (46%)</td>
<td>2.24 x 10$^{-3}$</td>
<td>1.34 x 10$^{-2}$</td>
<td>3.46 x 10$^{-4}$</td>
</tr>
</tbody>
</table>
Figure 7-3 and 7-4 shows scanning electron micrographs of the resultant anodic film surfaces formed on aluminium and AA 2024-T3 alloy respectively. The films were formed with the addition of 0.1 wt. % of the various fluoroacids. Porous surfaces were obtained at 0 °C for all fluoroacids and both substrates. Anodic films formed on aluminium with the addition of fluoroacids at 20 °C resulted in a collapsed cell structure apart from the film formed with the addition of 0.1 wt.% fluorozirconic acid which showed a porous structure. Anodic films formed on AA 2024-T3 alloy at 20 °C with fluoroacids showed a relatively intact porous surface excluding the film formed in fluorozirconic acid that showed evidence of cell collapse.

Figure 7-3. Scanning electron micrographs (backscattered electrons) of the surfaces of anodic films formed on aluminium in 0.1 M H₂SO₄ at 0 °C (top row) and 20 °C (bottom row). A and E – control specimens anodized without fluoroacid; B and G – 0.1 wt.% fluoroacids; C and H – 0.1 wt.% fluorosilicic acid (FS); D and J – 0.1 wt.% fluoroboric acid (FB); E and K – 0.1% fluorotitanic acid (FT).
Figure 7-4. Scanning electron micrographs (backscattered electrons) of the surfaces of anodic films formed on AA 2024-T3 alloy in 0.1 M H$_2$SO$_4$ at 0 °C (top row) and 20 °C (bottom row). A and E – control specimens anodized without fluoroacid; B and G – 0.1 wt.% fluorozirconic acid (FZ); C and H – 0.1 wt.% fluorosilicic acid (FS); D and J – 0.1 wt.% fluoroboric acid (FB); E and K – 0.1% fluorotitanic acid (FT).

Figure 7-5. Scanning electron micrographs (secondary electrons) of the cross-sections of anodic films formed on aluminium in 0.1 M H$_2$SO$_4$ at 0 °C (top row) and 20 °C (bottom row A and E – control specimens anodized without fluoroacid; B and G – 0.1 wt.% fluorozirconic acid (FZ); C and H – 0.1 wt.% fluorosilicic acid (FS); D and J – 0.1 wt.% fluoroboric acid (FB); E and K – 0.1% fluorotitanic acid (FT).
Figure 7-6 Scanning electron micrographs (secondary electrons) of the cross-sections of anodic films formed on AA 2024-T3 alloy in 0.1 M H₂SO₄ at 0 °C (top row) and 20 °C (bottom row A and E – control specimens anodized without fluoroacid; B and G – 0.1 wt.% fluorozirconic acid (FZ); C and H – 0.1 wt.% fluorosilicic acid (FS); D and J – 0.1 wt.% fluoroboric acid (FB); E and K – 0.1% fluorotitanic acid (FT).

Figure 7-5 and 7-6 show micrographs of cross-sections of films formed on aluminium and AA 2024-T3 alloy, respectively, with 0.1 wt.% of the various fluoroacids. The charge density passed during anodizing under each condition and the film thickness measured from scanning electron micrographs of cross-sections are listed in Table 7-2. The thickness values of films that exhibited collapsed cell structures are shown in bold type.

The increments in the film thickness (i.e. (thickness of test specimen – the thickness of control specimen)/thickness of control specimen), due to additions of 0.1 wt. % fluorozirconic, fluorosilicic, fluoroboric and fluorotitanic acid were 1.6, 3.6, 4.8 and 3.9 at 0 °C, respectively, and 0.95, 2.4, 1.4 and 2.3 at 20 °C, respectively. The increments in the thickness of the anodic films formed on AA 2024-T3 alloy with the addition of 0.1 wt. % fluorozirconic, fluorosilicic, fluoroboric and fluorotitanic acid were about 2.5, 4.2, 4.4 and 3.9 at 0 °C, respectively, and 1.2, 1.0, 0.8 and 1.1 at 20 °C, respectively, as shown in Table 7-2.

Additions of 0.1 wt.% fluorozirconic, fluorosilicic, fluoroboric and fluorotitanic acid to 0.1 M sulphuric acid increased the charge density relative to the aluminium control specimen by factors of about 2.5, 4.2, 5.2 and 4.9 at 0 °C, respectively, and by factors of about 2.1, 3.6, 4.7 and 3.4 at 20 °C. The ratio of the film thickness to the charge density was in the
range 0.45 to 0.51 nm cm\(^2\) mC\(^{-1}\) for specimens anodized at 0 °C, including the control specimens. The similarity of the values suggests a negligible loss of film thickness due to chemical dissolution in the presence all the fluoroacids. Also anodizing of AA 2024-T3 alloy with the addition of fluoroacids increased the charge density relative to the control specimen by factors of about 2.0, 2.7, 2.7 and 3.0 at 0 °C, respectively, and by factors of about 2.0, 1.7, 1.5 and 2.7 at 20 °C. The ratio of the film thickness to the charge density was in the range 0.26 to 0.32 nm cm\(^2\) mC\(^{-1}\) for specimens anodized at 0 °C, excluding the control specimens 0.19 nm cm\(^2\) mC\(^{-1}\), this low value of the control specimen could be due the influence of intermetallic particles on the etched alloy surface on oxygen evolution in the early stages of anodizing. The similarity of the charges density values suggested a negligible loss of film thickness due to chemical dissolution in the presence all the fluoroacids.

The largest increment in the film thickness relative to the control specimen and the thickest film was obtained with 0.1 wt. % fluoroboric acid at 0 °C, although with the collapse of the cell structure, 0.1 wt.% fluorosilicic produced the highest increment at 20 °C. Cell collapse was a feature of films formed at 20 °C in electrolytes containing fluoroboric acid, fluorosilicic acid or fluorotitanic acid.

The various fluoroacids additions have similar effects on the anodizing process, increasing the anodic film thickness and current density. However, the anodic films exhibit some difference in the surface morphology, charge density, and cross-section thickness, due to the difference in fluoroacid type, concentration, anodizing time and temperature.
Table 7.2. Thicknesses of films, determined by SEM, and charge density passed for anodizing of aluminium and AA 2024-T3 alloy for 1200 s at 22 V in 0.1 containing 0.1 wt.% fluoroacids at 0 °C and 20 °C. The thickness values in bold type are for films with a collapsed porous structure at the film surface.

<table>
<thead>
<tr>
<th>Addition %</th>
<th>0.1 M sulphuric acid</th>
<th>0.1% Fluorozirconic</th>
<th>0.1% Fluoroboric</th>
<th>0.1% Fluorosilicic</th>
<th>0.1% Fluorotitanic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Aluminium AA2024</td>
<td>Aluminium AA2024</td>
<td>Aluminium AA2024</td>
<td>Aluminium AA2024</td>
<td>Aluminium AA2024</td>
</tr>
<tr>
<td>Film thickness (µm)</td>
<td>0.22 ± 0.02</td>
<td>0.58 ± 0.02</td>
<td>1.28 ± 0.01</td>
<td>1.01 ± 0.02</td>
<td>1.08 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>0.16 ± 0.01</td>
<td>0.49 ± 0.02</td>
<td>0.76 ± 0.02</td>
<td>0.73 ± 0.01</td>
<td>0.69 ± 0.01</td>
</tr>
<tr>
<td>Charge density (C/cm²)</td>
<td>0.486</td>
<td>0.881</td>
<td>1.232</td>
<td>2.518</td>
<td>2.027</td>
</tr>
<tr>
<td></td>
<td>0.881</td>
<td>1.805</td>
<td>2.392</td>
<td>2.369</td>
<td>2.624</td>
</tr>
<tr>
<td>Ratio (µm cm²/C)</td>
<td>0.45</td>
<td>0.47</td>
<td>0.51</td>
<td>0.50</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>0.27</td>
<td>0.32</td>
<td>0.3</td>
<td>0.26</td>
</tr>
<tr>
<td>(thick. 0 °C – control 0 °C) / control 0 °C</td>
<td>------</td>
<td>------</td>
<td>1.64</td>
<td>4.82</td>
<td>3.61</td>
</tr>
<tr>
<td></td>
<td>------</td>
<td>------</td>
<td>2.5</td>
<td>4.43</td>
<td>4.2</td>
</tr>
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<td></td>
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<td>3.61</td>
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<td>------</td>
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<td>2.5</td>
<td>4.2</td>
<td>3.92</td>
</tr>
<tr>
<td>0 °C</td>
<td>2.147</td>
<td>4.607</td>
<td>10.106</td>
<td>3.908</td>
<td>7.802</td>
</tr>
<tr>
<td></td>
<td>2.548</td>
<td>5.018</td>
<td>7.001</td>
<td>4.227</td>
<td>7.376</td>
</tr>
<tr>
<td></td>
<td>0.44</td>
<td>0.40</td>
<td>0.31</td>
<td>0.40</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>0.22</td>
<td>0.25</td>
<td>0.27</td>
<td>0.27</td>
<td>0.17</td>
</tr>
<tr>
<td>20 °C</td>
<td>3.27</td>
<td>2.16</td>
<td>1.55</td>
<td>0.73</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td>3.07</td>
<td>0.73</td>
<td>0.37</td>
<td>0.59</td>
<td>1.88</td>
</tr>
<tr>
<td></td>
<td>3.27</td>
<td>1.55</td>
<td>2.11</td>
<td>0.74</td>
<td>0.74</td>
</tr>
</tbody>
</table>
7.2.2 Film compositions: EDX spectroscopy

EDX analyses were carried out of the films formed on aluminium for 300 s at 0 and 20 °C with additions of a fluoroacid. The EDX results are given in Table 7-3. The atomic ratios of S:Al in the films formed with additions of 0.1 wt.% of the different fluoroacids was in the range 0.05 to 0.07. They did not depend significantly on either the temperature of the electrolyte, the type of fluoroacid or the concentration of the fluoroacid. The S:Al ratio is consistent with a ratio of about 0.07 to 0.08 that has been reported in films formed using a higher sulphuric acid concentration of 3 wt.% at 0 °C [222]. The average S:Al ratio and sulphur concentration for all of the specimens anodized using fluoroacids were 0.06 and 2.2 at.% respectively. For additions of 0.1 wt.% fluoroacid at 0 °C, the F:Al ratio increased in order fluorozirconic acid, fluorosilicic acid, fluoroboric acid, fluorotitanic acid, ranging from 0.06 to 0.11 at 0 °C. The fluorine concentration increased from 2.6 at.% with fluorozirconic acid to 4.0 at.% with fluorotitanic acid. At 20 °C, the ranking was modified: fluorozirconic acid < fluorosilicic acid < fluoroboric acid ≈ fluorotitanic acid, with a range from 0.07 to 0.10. The fluorine concentrations increased from 2.7 at.% with fluorozirconic acid to 3.5 at.% with fluoroboric acid.

Table 7-3. Results of EDX analyses of anodic films formed on aluminium for 300 s at 22 V in 0.1 M H$_2$SO$_4$ containing different concentrations of fluoroacids or sodium fluoride at 0 °C and 20 °C.

<table>
<thead>
<tr>
<th>Fluoroacid type and wt. %</th>
<th>F (at. %)</th>
<th>S (at. %)</th>
<th>F:Al</th>
<th>S:Al</th>
<th>F (at. %)</th>
<th>S (at. %)</th>
<th>F:Al</th>
<th>S:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 wt.% fluorozirconic acid</td>
<td>2.6</td>
<td>2.2</td>
<td>0.064</td>
<td>0.056</td>
<td>2.7</td>
<td>2.1</td>
<td>0.072</td>
<td>0.057</td>
</tr>
<tr>
<td>0.1 wt.% fluorosilicic acid</td>
<td>2.8</td>
<td>2.2</td>
<td>0.070</td>
<td>0.056</td>
<td>3.3</td>
<td>2.3</td>
<td>0.089</td>
<td>0.061</td>
</tr>
<tr>
<td>0.1 wt.% fluoroboric acid</td>
<td>3.4</td>
<td>2.2</td>
<td>0.095</td>
<td>0.061</td>
<td>3.6</td>
<td>2.2</td>
<td>0.097</td>
<td>0.059</td>
</tr>
<tr>
<td>0.1 wt%. fluorotitanic acid</td>
<td>4.0</td>
<td>2.2</td>
<td>0.110</td>
<td>0.061</td>
<td>3.5</td>
<td>2.3</td>
<td>0.096</td>
<td>0.062</td>
</tr>
<tr>
<td>0.5 wt.% fluorozirconic acid</td>
<td>4.9</td>
<td>2.4</td>
<td>0.135</td>
<td>0.068</td>
<td>5.3</td>
<td>2.2</td>
<td>0.142</td>
<td>0.060</td>
</tr>
<tr>
<td>1.0 wt.% fluorozirconic acid</td>
<td>5.8</td>
<td>2.4</td>
<td>0.163</td>
<td>0.066</td>
<td>8.9</td>
<td>1.9</td>
<td>0.246</td>
<td>0.053</td>
</tr>
</tbody>
</table>
7.2.3 Film compositions: GDOES

Elemental depth profiles in the anodic films formed on aluminium were obtained by GDOES in order to demonstrate the presence of fluorine throughout the thicknesses of films formed for 300 s, thereby complementing the EDX analysis presented previously in Table 7-3. The profiling was restricted to films formed at 0 °C.

Figure 7-7. GDOES elemental profiles of aluminium anodized at 22 V for 300 s, in 0.1 M H_2SO_4 at 0 °C containing (a) no fluoroacid, (b) 0.1% fluorozirconic acid, (c) 0.1 wt.% fluorosilicic acid, (d) 0.1 wt.% fluoroboric acid and (e) 0.1 wt.% fluorotitanic acid. The aluminium, oxygen, boron and fluorine intensities were multiplied by factors of 5, 10, 10 and 1 respectively.
Results are presented in Figure 7-7 for the films formed with different fluoroacids. The aluminium/film interface coincides with the decline of the oxygen intensity and the rise of the aluminium intensity as sputtering of the substrate commences. The times required to sputter through the films formed using 0, 0.1% fluorozirconic acid, 0.1 wt.% fluorsilicic acid, 0.1 wt.% fluoroboric acid and 0.1 wt.% fluorotitanic acid, were about 6, 38, 33, 42 and 48 s, respectively, indicating an increasing thickness with additions of fluoroacids. Fluorine was present throughout the thickness of each film. The fluorine appeared to be distributed uniformly through most of the film thickness, with apparently no depletion with depth. Sulphur was present throughout most of the thickness of the films. The fluorine signal extended beyond the sulphur signal, which indicates the presence of a sulphur-free, fluorine-containing layer at the base of the films.

Figure 7-8. GDOES elemental profiles of aluminium anodized at 22 V for 300 s, in 0.1 M H_2SO_4 at 0 °C, (a) 0.1, 0.5 and 1.0% fluorozirconic acid, (b) 0.1, 0.5 and 1.0% fluorsilicic acid, (c) 0.1, 0.5 and 1.0% fluoroboric acid (d) 0.1, 0.5 and 1.0% fluorotitanic acid. The profiles in the respective figures show the signal intensities at the wavelengths selected for detection of zirconium, silicon, boron and titanium.
Figure 7-8 (a, b, c and d) shows the effect of increasing of the fluoroacid concentration on the GDOES signal intensities at the wavelengths selected for detection of zirconium, silicon, boron and titanium in films formed with additions of 0.1, 0.5 and 1.0 wt.% of the respective fluoroacids. No change in the intensities occurred in the film regions with an increase of the fluoroacid concentration. The decreases in all fluoroacids intensities at longer sputtering times are associated with a change in sputtering rate between the oxide and the aluminium substrate. The results indicate negligible incorporation of zirconium, silicon, boron and titanium in the films.

7.2.4 Film compositions: RBS

The titanium content in a film formed for 300 s, in 0.1 M sulphuric acid containing 0.1 wt.% fluorotitanic acid at 0 °C was measured by RBS.

![RBS spectra](image)

Figure 7-9 Experimental and simulated (solid line) RBS spectra for aluminium anodized at 0 °C in 0.1 M H₂SO₄ containing 0.1 wt.% fluorotitanic acid.

The resultant spectra revealed yields from oxygen, aluminium and sulphur, as shown in Figure 7-9. Comparison with a control specimen, anodized in the absence of fluoroacid, showed that only a pile-up background signal occurred in the energy range expected for titanium in the film. The upper limit on the Ti: Al atomic ratio was 1.5 x 10⁻³. The S: Al atomic ratio was about 0.055 in agreement with the results of the EDX analyses. The efficiency of anodizing was evaluated from the ratio of the charge due to the Al³⁺ ions in the film (7.76 x 10¹⁷ Al atoms cm⁻², 0.37 C cm⁻²) and the charge passed in the anodizing cell (0.60 C cm⁻²). The latter is consumed by oxidizing aluminium, with negligible contributions from side reactions, such as oxygen evolution. The charge ratio indicated that
the film formed at an efficiency of about 0.62. Films on control specimens anodized in fluoroacid free electrolytes at 0 °C formed at an efficiency of 0.63. The results suggest that the fluoroacid had negligible influence on the efficiency of oxidation of the aluminium and that dissolution of the film was also negligible.

7.2.5 Hardness measurements

Hardness measurements were made on specimens anodized for 1200, 2400 and 7200 s, in 0.1 M sulphuric acid containing 0.1 wt.% of fluoroboric acid, fluorosilicic acid, fluorotitanic acid or fluorozirconic acid. The electrolyte temperature was 0 °C. The results are presented in Table 7-4. Low values of the hardness of the control specimen at 1200 and 2400 s, 1.0 and 1.4 GPa resulted from the influence of the substrate on the hardness on the measured values due to the low thickness of the films (0.22 μm at 1200 s Table 7-2). Following the growth of a much thicker film after anodizing for 7200 s, the hardness was increased to 4.6 GPa. Apart from the specimen anodized for 1200 s with fluorozirconic acid, which resulted in a thin film (0.58 μm, Table 7-2), other films formed in the fluoroacid-containing electrolyte, which were of the thickness of ≥1 μm, revealed hardness values between 3.0 to 4.2 GPa following anodizing for either 1200 or 2400 s. However, the hardness decreased to very low values at 7200 s, which was due to the influences of chemical dissolution on the porous structure near the film surface.

Table 7-4. Results of hardness measurements made on aluminium anodized for 1200, 2400 and 7200 s, in 0.1 M sulphuric acid containing 0.1 wt.% fluoroacid at 0 °C.

<table>
<thead>
<tr>
<th></th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1200 s</td>
</tr>
<tr>
<td>Control</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>Fluoroboric acid</td>
<td>3.7 ± 0.1</td>
</tr>
<tr>
<td>Fluorosilicic acid</td>
<td>3.0 ± 0.2</td>
</tr>
<tr>
<td>Fluorotitanic acid</td>
<td>3.9 ± 0.2</td>
</tr>
<tr>
<td>Fluorozirconic acid</td>
<td>1.8 ± 0.1</td>
</tr>
</tbody>
</table>
The measured dissolution rate of the barrier layer in the film formed in the electrolyte containing fluorozirconic acid suggests that about 25% of the pore wall thickness may have been dissolved after anodizing for 7200 s. A greater loss may have occurred in practice due to a faster dissolution near the film surface owing to the easier transfer of species between the film and the bulk electrolyte.

### 7.2.6 Incorporation and distribution of fluorine

The presence of fluorine and the absence of born, silicon, titian and zirconium in the present films may be due to the following reactions:

\[
2\text{BF}_4^- + 3\text{H}_2\text{O} \rightarrow 2\text{F}^- + \text{B}_2\text{O}_3 + 6\text{HF}
\]  
7-1

\[
\text{SiF}_6^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{F}^- + \text{SiO}_2 + 4\text{HF}
\]  
7-2

\[
\text{TiF}_6^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{F}^- + \text{TiO}_2 + 4\text{HF}
\]  
7-3

\[
\text{ZrF}_6^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{F}^- + \text{ZrO}_2 + 4\text{HF}
\]  
7-4

Or

\[
\text{BF}_4^- \rightarrow \text{BF}_n^{(3-n)} + (4-n)\text{F}^-
\]  
7-5

\[
\text{SiF}_6^{2-} \rightarrow \text{SiF}_n^{(4-n)} + (6-n)\text{F}^-
\]  
7-6

\[
\text{TiF}_6^{2-} \rightarrow \text{TiF}_n^{(4-n)} + (6-n)\text{F}^-
\]  
7-7

\[
\text{ZrF}_6^{2-} \rightarrow \text{ZrF}_n^{(4-n)} + (6-n)\text{F}^-
\]  
7-8

The oxide species produced in reaction (7-1 to 7-4) may dissolve in the electrolyte or \(\text{B}^{3+}\), \(\text{Si}^{4+}\), \(\text{Ti}^{4+}\) and \(\text{Zr}^{4+}\) may be ejected from the film surface under the influence of the electric field. HF may be released to the electrolyte and could attack the film, or provide a source of fluoride for incorporation into the film. Fluoride ions produced by progressive dissociation of fluoroacids anions, according to reactions (7-5 to 7-8), may be directly
incorporated into the film. The subsequently generated $\text{BF}_2^+$, $\text{SiF}_3^+$, $\text{TiF}_3^+$ and $\text{ZrF}_3^+$ may migrate away from the film surface.

Alternatively, the following reactions may occur:

$$\text{BF}_4^- + \text{H}^+ \rightarrow \text{BF}_3^- + \text{HF} \quad 7-9$$

$$\text{BF}_3^- + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \rightarrow \text{BOF}^+ + 2\text{HF} \quad 7-10$$

$$\text{SiF}_6^{2-} + \text{H}^+ \rightarrow \text{SiF}_5^- + \text{HF} \quad 7-11$$

$$\text{SiF}_5^- + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{SiOF}^+ + 4\text{HF} \quad 7-12$$

$$\text{TiF}_6^{2-} + \text{H}^+ \rightarrow \text{TiF}_5^- + \text{HF} \quad 7-13$$

$$\text{TiF}_5^- + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{TiOF}^+ + 4\text{HF} \quad 7-14$$

$$\text{ZrF}_6^{2-} + \text{H}^+ \rightarrow \text{ZrF}_5^- + \text{HF} \quad 7-15$$

$$\text{ZrF}_5^- + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{ZrOF}^+ + 4\text{HF} \quad 7-16$$

The charge on the $\text{BOF}^+$, $\text{SiOF}^+$, $\text{TiOF}^+$ and $\text{ZrOF}^+$ should also cause them to migrate from the oxide surface.

The fluoride ions generated by the reactions are incorporated into the films. The HF may be released to the electrolyte. Alternatively, either HF may also provide fluoride ions for incorporation into the film, with the release of $\text{H}^+$ ions to the electrolyte.

Studies of barrier-type films have shown that $\text{Ti}^{4+}$ [262] and $\text{Zr}^{4+}$ [254] ions migrate at rates slightly greater than and similar to $\text{Al}^{3+}$ ions respectively, while $\text{B}^{3+}$ [182] and $\text{Si}^{4+}$ [92] ions are immobile. The migrations behaviours of cation species have been related to the strengths of the respective metal ion-O single bonds relative to the $\text{Al}^{3+}$-O bond [216]. In the absence of film growth at the pore base by outward migration of $\text{Al}^{3+}$ ions, such species are not expected to be present in porous films. It is also possible that fluoroacid anions dissociate directly under the electric field at the pore bases, according to the reactions:
The fluoride ions are incorporated into the film and the cation species are then ejected to the electrolyte.

The magnitudes of the current density did not reveal a consistent dependence in the fluoroacid type for anodizing of the alloy and aluminium in the presence of fluoroacids.

However, in general, the presence of fluorozirconic acid tended to result in a lower current density compared with other fluoroacid additions, and the film formed using fluorozirconic acid contained the lower concentration of fluorine. This electrolyte also had the lower amount of bonded fluorine and the second lower amount of free fluorine. In contrast, fluorotitanic acid contained relatively high concentrations of both bonded and free fluoride and anodizing in the presence of fluorotitanic acid tended to result in increased current density and a higher concentration of fluorine in the film.

### 7.3 Conclusions

1. Similar to fluorozirconic acid additions of fluorosilicic, fluoroboric and fluorotitanic acid to sulphuric acid increase the growth rate of anodic films formed on aluminium and AA 2024-T3 alloy under a constant voltage of 22 V at 0 and 20 °C. The effect of the fluoroacid addition on the increment in film thickness is greater at 0 °C than at 20 °C.

2. The films contain oxide, sulphate and fluoride species. Metal species of the fluoroacid anions are not incorporated into the films. The incorporation of fluoride ions has negligible influence on the concentration of incorporated sulphate ions.

3. The addition of fluoroacids to sulphuric acid increases the rate of film growth during anodizing of aluminium and AA 2024-T3. The increments in the growth rate may be offset by increased chemical dissolution, leading to collapse of the cell structure and film thinning, especially at a higher temperature and sulphuric acid concentration.

\[
\begin{align*}
\text{BF}_4^- & \rightarrow 4\text{F}^- + \text{B}^{3+} & \text{7-17} \\
\text{SiF}_6^{2-} & \rightarrow 6\text{F}^- + \text{Si}^{4+} & \text{7-18} \\
\text{TiF}_6^{2-} & \rightarrow 6\text{F}^- + \text{Ti}^{4+} & \text{7-19}
\end{align*}
\]
8 Summary and the future work

8.1 Introduction

Limited information is available in the Literature regarding the influence of fluorine ions on anodic films generated on aluminium and aluminium alloys; most research on influences of fluorine in anodizing is focussed on studying films with a nanotubular morphology generated on titanium. In the present research, a barrier layer and porous anodic films were formed on aluminium and examined using advanced analytical techniques. Special attention was given to the study of the influence of fluorine ions added to the electrolyte and film growth rates, morphologies, structures and compositions of the anodic films.

The main aim in the present study verified by addition of fluorine ions which cause an increment in the anodic film growth rate and consequence to that practical benefits could be achieved in the anodizing process, such as minimize the anodizing time and energy.

8.2 Summary

The effect of the bonded and free fluoride ions on aluminium and AA 2024-T3 alloy was investigated by adding sodium fluoride and fluoroacids to sulphuric acid and sulphuric/tartaric acid; the study employed different anodizing temperatures, voltages, times, addition type and addition concentrations.

Study the effect of fluoride addition on the barrier layer revealed that additions of sodium fluoride led to the incorporation of fluoride ions into the anodic film, and the incorporated fluoride ions migrated inwards at about twice the rate of O\(^2\) ions. Consequently, a fluoride-enriched layer is formed at the base of the film. Fluoride ions can promote the field-assisted ejection of Al\(^{3+}\) ions from the surface of the anodic film, thereby reducing the efficiency of film growth.

To understand the role of the fluorine species in the anodic film, fluorozirconic acid and sodium fluoride were added to the sulphuric acid. The results showed increases in the growth rate of anodic films formed on aluminium under a constant voltage of 22 V at 0 and 20 °C. The effect of the fluoroacid addition on the increment in film thickness is greater at 0 °C than at 20 °C. The growth rates of the films decrease with time of anodizing since
diffusion controls the supply of fluoroacid anions and fluoride ions to the base of pores. Increasing the concentration of the fluoroacid or sodium fluoride increases the growth rate. However, film dissolution is also enhanced. This can lead to the collapse of the porous structure at the film surface, which is promoted by increased fluoroacid/fluoride concentration and electrolyte temperature. The films contain oxide, sulphate and fluoride species. Zirconium species are not incorporated into the films formed in electrolytes containing fluorozirconic acid. The incorporation of fluoride ions has negligible influence on the concentration of incorporated sulphate ions.

Further investigation was carried out by adding of 0.1 wt.% fluorozirconic acid to a mixed 0.53 M tartaric acid/0.4 sulphuric acid, the results show increases the rate of film growth by a factor of about 2.3 during anodizing at 14 or 18 V at 0 °C for times up to 7200 s. The factor reduces to significantly at 20 °C, to roughly 1.2. At 37 °C, no significant thickness enhancement occurs. The addition of fluorozirconic to TSA enhances the rate of chemical dissolution of the film. However, although pore widening may occur, no loss of film thickness occurred for films formed for times up to 7200 s at 0 °C or for films formed for 1560 s at 20 and 37 °C. Anodizing for 7200 s, at 20 and 37 °C led to the collapse of the cell structure in the outer region of the films due to pore wall thinning. Fluoride and sulphate ions from the electrolyte are incorporated into the anodic alumina. The concentration of the fluoride ion in the film decreases with increasing temperature. However, the concentration of sulphate is not significantly changed.

Investigation of the effect of different fluoroacid types on anodic film formation on aluminium and AA 2024-T3 alloy revealed relatively small differences in the film surface morphology, charge density passed to form the films, and film thickness due to the different fluoroacid types. Similar to fluorozirconic acid additions of a fluorosilicic, fluoroboric and fluorotitanic acid to sulphuric acid increase the growth rate of anodic films formed on aluminium and AA 2024-T3 alloy under a constant voltage of 22 V at 0 and 20 °C. The effect of the fluoroacid addition on the increment in film thickness is greater at 0 °C than at 20 °C.
8.3 Novelty of the study

The current study provides new information about the effect of fluoride ions and fluoroacid species on the anodizing of aluminium and aluminium alloys, which is not available in the current literature. Key new findings include:

- the effect of fluorine species on the anodizing efficiency, film morphology and film composition;
- the amounts of fluoride ions and fluoroacids species in film and the migration behaviour of fluoride in anodic alumina;
- the effect of fluorine species on film dissolution;
- the effect of fluoroacids concentration and type; electrolyte concentration and temperature on the film growth rate;
- differences in anodizing behaviours of aluminium and aluminium alloy due to the presence of alloying elements.

8.4 Future work and plan

- The present study revealed that addition of a certain amount of fluoride ions to ammonium pentaborate created a porous film. However, the exact fluoride ion concentration for the transition was not determined. The critical concentration can be identified by anodizing using a wider range of electrolyte compositions.
- The current study used sulphuric acid and sulphuric/tartaric acid as control acids with fluoride ion and fluoroacid additions made to enhance the anodic film growth on aluminium and AA 2024-T3 alloy substrate. The fluorine species result in etching of the film surface, which may be beneficial to adhesive bonding or retention of paint layers. This could be investigated using films formed in the present acids and in oxalic acid or phosphoric acid, which enable anodizing to higher potentials.
- This study showed the incorporation of fluoride ions into barrier-type films; the fluoride ions migrated inwards in anodic alumina at about twice the rate of $O^{2-}$ ions and a fluoride-rich layer was present next to the substrate. A fluoride-rich layer was proposed to be present at the cell boundaries in the anodic film; this result could be examined in more detail by creating larger cells using phosphoric or oxalic acid which allows anodizing to high voltage and would facilitate the examination of the film by TEM to identify the location of the fluoride-rich layer at the cell boundaries.
• Study of the effect of the fluoride-rich layer at the film base on adhesive of the film to the substrate eg by measuring the force required to detach the film.

• Investigation of the effect of a dipping the post-treatment in the fluoroacids solutions of anodized specimens on the corrosion resistance provided by sealed and unsealed anodic films.

• Optimize the temperature, voltage and fluorozirconic acid concentration for accelerating film growth relative to control film, while minimizing film dissolution.

• Further study could be carried out to determine the effect of fluorine ions in the barrier, by immersion of the aluminium and aluminum alloy in hydrofluoric acid to incorporate fluoride in a thin initial oxide layer followed by anodizing the specimens in the control electrolyte, any change in the fluoride-enriched layer could be identify by using XPS after remove the metal substrate.

• Modified deoxidizing parameters by adding the fluorine ions to the electrolytic phosphoric acid deoxidizing (EPAD), then anodizing in the control electrolyte.

• In order to produce a thicker anodic film with good adherent and corrosion properties duplex anodic film layer could be formed by anodizing the dilute aluminium alloy in phosphoric acid with fluoroacids addition and then anodizing in sulphuric acid.

• Further study could be carried out to identify possible practical benefits of adding fluorine species to sulphuric acid in the hard anodizing process, such as increasing the film growth rate subsequently minimizes the anodizing energy and extends the electrolyte bath lifetime.
9 References


[185] A.P. 02-01-003, Tartaric sulphuric acid anodizing, in, API.


