Influence of Fluorozirconic Acid on Sulfuric Acid Anodizing of Aluminum

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The effects of additions of fluorozirconic acid to sulfuric acid on the anodizing behavior of aluminum have been investigated under a constant voltage at temperatures of 0 and 20°C. The fluorozirconic acid increased the rate of film growth, with a dependence on the fluorozirconic concentration, the electrolyte temperature and the anodizing time. Compositional analyses showed that fluorine species were present in the films. However, zirconium species were absent. The fluorozirconic acid generally enhanced film dissolution, although this effect was less important at low fluorozirconic concentration, low electrolyte temperature and short anodizing times. Sodium fluoride additions influenced the anodizing behavior similarly to the fluorozirconic acid.

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Chromium (VI)-free conversion treatments that include fluorotanic and fluorozirconic acids in the bath formulations have been developed for aluminum alloys.1−6 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 aluminum oxyfluorides, oxides and hydroxides, which constitute the main part of the coating thickness. In comparison with the findings from the relatively numerous studies of conversion coatings produced using fluoride next to the substrate. In comparison with the findings from the relatively numerous studies of conversion coatings produced using fluoride next to the substrate. In comparison with the findings from the relatively numerous studies of conversion coatings produced using fluoride next to the substrate. In comparison with the findings from the relatively numerous studies of conversion coatings produced using fluoride next to the substrate.

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Specimens of size 3 cm x 2 cm were cut from a 99.99% aluminum foil of 0.3 mm thickness. They were then electropolished for 3 min in a mixture of 60% perchloric acid and ethanol, with a volume ratio of 20:80, at 278 K. After rinsing in ethanol and distilled water and application of a lacquer mask (Stopper 45 McDermid) to define a working area on one side of 2 cm², anodizing was carried out at 22 V for 300 s, at 25°C, 500 and 1200 s at 0 or 20°C in 0.1 M sulfuric acid containing 0.1, 0.5, 1.0 wt% of 46% fluorozirconic acid (H2ZrF6). The fluorozirconic acid containing free-fluoride, with a concentration of 10−2 mol dm−3 as measured by the supplier (Almetron Ltd). The molar concentrations of the fluorozirconic acid and free-fluoride in the prepared electrolytes are given in Table I. Electrolytes were also prepared using 0.1 M sulfuric acid with additions of sodium fluoride (NaF – Fisher scientific 99.0+ %) at concentrations from 3.5 × 10−3 M to 3.5 × 10−2 M that were selected to cover the concentrations of total fluoride and free-fluoride in the fluorozirconic acid-containing electrolytes. As well as anodizing in electrolytes prepared with 0.1 M sulfuric acid, films were also formed at 22 V in 1.0 M sulfuric acid at 0 or 20°C with and without addition of 0.1 wt% fluorozirconic acid.

A two electrode cell was used for anodizing individual specimens, with a cylindrical aluminum 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.

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. Compositional analysis of films

| FZ addition to 0.1 M H2SO4 | FZ concentration | Total fluorine concentration | Free fluoride |
|---------------------------|------------------|-----------------------------|--------------|
| (wt%)                     | mol. dm−3        |                             |              |
| 0.1                       | 2.24 × 10−3      | 1.34 × 10−2                 | 3.46 × 10−4  |
| 0.5                       | 1.12 × 10−2      | 6.72 × 10−2                 | 1.73 × 10−3  |
| 1.0                       | 2.24 × 10−2      | 1.34 × 10−1                 | 3.46 × 10−3  |

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Experimental

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| 1.0                       | 2.24 × 10−2      | 1.34 × 10−1                 | 3.46 × 10−3  |

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was carried out using energy-dispersive X-ray (EDX) analysis (Ox-  
ford Instrument XMAX 80) in a 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 aluminum in the substrate. Se-  
lected specimens were also analyzed 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%.  

Transmission electron microscopy (TEM) of selected specimens  
was carried out using an FEI-Philips CM202 instrument, operated at  
200 kV. 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.  

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 (aluminum), 130.217 nm  
(oxygen), 685.602 nm (fluorine) and 339.197 nm (zirconium).  

Results  
Current density-time curves and film morphologies.—The effects  
of fluorozirconic acid additions on the current density-time curves  
during anodizing of aluminum in 0.1 M sulfuric acid for 1200 s at a  
constant voltage of 22 V are presented in Figures 1a and 1b for temper-  
atures 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 elec-  
trolyte. The insets in Figure 1 show the trends in the current density  
during the first 100 s of anodizing. A peak current density occurred  
for all specimens immediately on the application of the voltage due to  
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. For the control specimens, a  
steady current density associated with the growth of the major pores  
was subsequently achieved. In contrast, the presence of the fluoroacid  
led to a second peak in the current density, followed by a slow decline  
toward a steady value. The second peak occurred at an earlier time  
with increase of the concentration of the fluoroacidic acid, suggest-  
ing that the fluoroacid assisted the establishment of major pores. The  
effect of the concentration of sulfuric acid on the anodizing behavior  
was investigated using a 1.0 M sulfuric 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  
1c, which also includes the curves for the fluoroacid-free solution.  
Similarly to the observations made with the 0.1 M sulfuric acid, the  
current density was enhanced by the fluoroacid, with the effect tending  
to decrease with increasing anodizing time.  

Figure 2 shows scanning electron micrographs of the resultant film  
surfaces. Porous surfaces were obtained at 0 °C for all fluoroacidic  
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 3. The film thickness measured from the micrographs  
and the charge density passed in forming the films are listed in Table II.  
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 – 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 sulfuric 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.  
The thickness values of films that exhibited collapsed cell struc-  
tures are shown in bold type in Table II. Additions of 0.1, 0.5 and 1.0  
wt% fluorozirconic acid to 0.1 M sulfuric acid increased the charge  
density relative to the control specimen by factors of about 2.5, 7.5
Figure 2. Scanning electron micrographs (backscattered electrons) of the surfaces of anodic films formed on aluminum 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.

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 nm cm² mC⁻¹ for specimens anodized at 0°C, including the control specimens. The similarity of the values suggests 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 nm cm² mC⁻¹ 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 sulfuric 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.

Figure 3. Scanning electron micrographs (secondary electron electrons) of the cross-sections of anodic films formed on aluminum 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.
Table II. Thicknesses of films, determined by SEM, and charge density passed for anodizing of aluminum for 1200 s at 22 V in 0.1 and 1.0 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.

| FZ (wt%) | 0.1 M H₂SO₄ | 1.0 M H₂SO₄ |
|---------|-------------|-------------|
|         | 0 | 0.1 | 0.5 | 1.0 | 0 | 0.1 |
| 0°C     | Film thickness (μm) | 0.22 ± 0.02 | 0.58 ± 0.02 | 1.68 ± 0.02 | 1.97 ± 0.02 | 2.01 ± 0.02 | 4.62 ±0.03 |
|         | Charge density (C/cm²) | 0.486 | 1.232 | 3.646 | 4.013 | 4.284 | 10.091 |
|         | Ratio (μm cm²/C) | 0.45 | 0.47 | 0.46 | 0.49 | 0.47 | 0.46 |
| 20°C    | Film thickness (μm) | 0.94 ± 0.01 | 2.02 ± 0.01 | 2.61 ± 0.05 | 2.90 ± 0.16 | 13.51 ± 0.02 | 16.91 ± 0.01 |
|         | Charge density (C/cm²) | 2.147 | 4.607 | 12.837 | 25.691 | 26.646 | 31.932 |
|         | Ratio (μm cm²/C) | 0.44 | 0.40 | 0.20 | 0.11 | 0.51 | 0.53 |

Figure 4. Bright field transmission electron micrographs of ultramicrotomed cross-sections of aluminum 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 4 presents bright field transmission electron micrographs of films formed for 300 and 1200 s in 0.1 M sulfuric 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 1a. The latter growth rate compares satisfactorily with a rate of 0.48 nm s⁻¹ calculated using the film thickness of Table II 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 sulfuric acid.¹⁰ A similar barrier layer thickness was observed in a specimen anodized in the fluorozirconic acid-free electrolyte (not shown).

Sodium fluoride had a generally similar effect on the anodizing curves as the fluorozirconic acid: the charge density at 0°C increased progressively with additions of 3.5 × 10⁻³, 3.5 × 10⁻² and 3.5 × 10⁻¹ M sodium fluoride by factors of about 4.2, 6.4 and 8.8 at 0°C (Table III). 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 × 10⁻³ and 3.5 × 10⁻² M at 0°C, and to 3.5 × 10⁻³ M at 20°C. Disintegration of the porous structure due to chemical dissolution occurred for 3.5 × 10⁻¹ M at 0°C, and collapse of the structure at 3.5 × 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 cm² mC⁻¹ at 0°C, but was reduced by film dissolution to the range 0.38 to 0.26 nm cm² 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 of 3.5 × 10⁻³, 3.5 × 10⁻² and 3.5 × 10⁻¹ M sodium fluoride, respectively, and of 0.36, 1.86 at 20°C for additions of 3.5 × 10⁻³ and 3.5 × 10⁻² M sodium fluoride.

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 × 20 μm. Aluminum, oxygen, sulfur 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

| NaF (M) | 0 | 3.5 × 10⁻³ | 3.5 × 10⁻² | 3.5 × 10⁻¹ |
|---------|---|-------------|-------------|-------------|
| 0°C     | Film thickness (μm) | 0.22 ± 0.02 | 0.91 ± 0.01 | 1.65 ± 0.01 | 1.99 ± 0.01 |
|         | Charge density (C/cm²) | 0.486 | 2.026 | 3.096 | 4.261 |
|         | Ratio (μm cm²/C) | 0.45 | 0.44 | 0.54 | 0.46 |
| 20°C    | Film thickness (μm) | 0.94 ± 0.01 | 1.28 ± 0.02 | 2.69 ± 0.01 | n.d. |
|         | Charge density (C/cm²) | 2.147 | 3.341 | 10.175 | n.d. |
|         | Ratio (μm cm²/C) | 0.44 | 0.38 | 0.26 | n.d. |

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confirms that the amount of incorporated zirconium was negligible. The results of averages of typically three analyses of each specimen are given in Table IV. 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 fluorooxide. 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 sulfuric acid concentration of 3 wt% at 0°C. The average S:Al ratio and sulfur concentration for all of the specimens anodized using fluorooxide 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.%. The analysis of fluorine for a sodium fluoride concentration of 3.5 × 10⁻³ M sodium fluoride required the use of a lower electron beam energy to avoid significant interference from the aluminum substrate. This precluded measurement of the sulfur concentration.

The O:Al ratio was similar for all specimens anodized in the presence of fluorooxide and sodium fluoride, with an average value 1.50 and a range from 1.40 to 1.63. A typical film formed using fluorooxide 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 Al₂O₃.0.04Al₂(SO₄)₃.0.07AlF₃.

In order to determine the distribution of fluorine, EDX analyses were also made at three locations in a cross-section of a film formed for 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 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 V. The fluorine concentration decreased by about 28% between the outer half of the film and the inner half of the film, whereas the sulfur 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 1b). The increase in the sulfur concentration may be a consequence of a

![Figure 5. Relationship between the F:Al atomic ratio in the film and the average current density during anodizing of aluminum 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.](image_url)

Table IV. EDX analyses of anodic films formed on aluminum for 300 s at 22 V in 0.1 M H₂SO₄ or 1.0 M H₂SO₄ 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).

| Electrolyte | F (at.%) 0°C | S (at.%) 0°C | S:Al | F (at.%) 20°C | S:Al |
|-------------|--------------|--------------|------|--------------|------|
| 0.1 wt% FZ  | 2.6          | 2.2          | 0.06 | 6.5          | 5.5  |
| 0.5 wt% FZ  | 4.9          | 2.4          | 0.14 | 9.3          | 5.7  |
| 1.0 wt% FZ  | 5.8          | 2.4          | 0.16 | 9.7          | 5.6  |
| 3.5 × 10⁻³ M NaF | 1.7 | n.d. | 0.04 | 1.0 | 0.33 |
| 3.5 × 10⁻² M NaF | 3.2 | 2.7 | 0.08 | 2.1 | 0.22 |
| 3.5 × 10⁻¹ M NaF | 12.9 | 1.9 | 0.37 | 7.4 | 2.2 |

| Electrolyte | F (at.%) 0°C | S (at.%) 0°C | S:Al | F (at.%) 20°C | S:Al |
|-------------|--------------|--------------|------|--------------|------|
| 0.1 M H₂SO₄| 1.0          | 3.5          | 0.03 | 6.5          | 5.5  |
| 0.5 M H₂SO₄| 2.6          | 2.2          | 0.06 | 6.5          | 5.5  |
| 1.0 M H₂SO₄| 4.9          | 2.4          | 0.14 | 9.3          | 5.7  |

Table V. EDX analyses of a cross-section of an anodic film formed on aluminum for 1200 s at 22 V in 0.1 M H₂SO₄ containing 1.0 wt% fluorozirconic acid 20°C.

| Region         | Analysis 1 F (at.%) | Analysis 1 S (at.%) | Analysis 2 F (at.%) | Analysis 2 S (at.%) |
|----------------|---------------------|---------------------|---------------------|---------------------|
| Outer region   | 7.9                 | 1.5                 | 6.5                 | 1.9                 |
| Middle region  | 5.7                 | 2.2                 | 5.5                 | 1.9                 |
| Inner region   | 5.0                 | 2.3                 | 5.4                 | 2.5                 |
The reduced concentration of fluorine species in the electrolyte within the pores that enables an increase in incorporation of sulfate ions into the film.

**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 for 300 s, thereby complementing the EDX analysis presented previously in Table IV. The profiling was restricted to films formed at 0°C. Results are presented in Figure 6 for the films formed with different concentrations of fluorozirconic acid. The aluminum/film interface coincides with the decline of the oxygen intensity and the rise of the aluminum 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 as 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 with 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 V). The absence of depletion is probably a consequence of faster diffusion of fluorine in the pores of the thinner films analyzed by GDOES, and possibly also of changes in the sputtering rate of the film during profiling. Sulfur was present throughout most of the thickness of the films. The fluorine signal extended beyond the sulfur signal, which indicates the presence of a sulfur-free, fluorine-containing layer at the base of the films. Optical emission intensities at the wavelength for zirconium (not shown) were at the background level, indicating negligible amounts of zirconium in the films.

**Film compositions: RBS.**—The zirconium content in a film formed for 300 s in 0.1 M sulfuric 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 spectrum revealed yields from oxygen, aluminum and sulfur, as shown in Figure 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 × 10⁻³. The Zr/S 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 × 10⁻⁴. The Zr/S ratio was therefore lower by a factor ≥ 28 than the molar ratio of fluorozirconate ions to sulfate ions in the electrolyte (2.24 × 10⁻²). The efficiency of anodizing was evaluated from the ratio of the charge due to the Al³⁺ ions in the film (276 mC cm⁻²) and the charge passed in the anodizing cell (402 mC cm⁻²). The latter is consumed by oxidizing aluminum, 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 aluminum. The dissolution of the film was also negligible. In contrast, it was reported previously that the efficiency of oxidation of the aluminum was reduced progressively by increasing additions of ammonium hexafluorosilicate or ammonium fluoride to oxalic acid. After anodizing for 90 min, at a temperature of 17°C, and an ammonium hexafluorosilicate 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.

**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 sulfuric 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 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 VI. 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 72 and 74 kJ mol$^{-1}$ are indicated for the respective solutions. 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 predicted 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 deionized 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

| FZ (wt%) | Temperature (°C) | Dissolution rate (nm s$^{-1}$) | Intercept (nm) |
|---------|------------------|-------------------------------|----------------|
| 0.1     | 0                | 2.3 $\times$ 10$^{-4}$       | 19.5           |
| 0.1     | 20               | 2.0 $\times$ 10$^{-3}$       | 20.1           |
| 1.0     | 0                | 2.5 $\times$ 10$^{-3}$       | 18.3           |
| 1.0     | 20               | 2.3 $\times$ 10$^{-2}$       | 18.2           |

Table VI. Dissolution rates of the barrier layer in 0.1 M sulfuric acid containing either 0.1 or 1.0 wt% fluorozirconic acid (FZ) at 0 and 20°C.
Table VII. Porosities of films formed on aluminum 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.

| FZ wt% | 0    | 0.1  | 0.5  | 1.0  |
|--------|------|------|------|------|
| 0°C    | 11.9 | 11.1 | 14.7 | 17.1 |
| 20°C   | 17.5 | 19.2 | 18.1 |      |

60 s. For other electrolyte conditions, chemical dissolution is expected to be comparatively negligible.

**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, 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. Outward migration of Al$^{3+}$ was 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 VII. The porosities were not significantly affected by the temperature of the sulfuric acid electrolyte, but increased with additions of fluorozirconic acid, with values of about 11.5%, 14.2%, 17.3% and 18.6% for 0, 0.1, 0.5 and 1.0 wt% fluorozirconic acid.

**Incorporation and distribution of fluorine.**—Porous films are formed by inward migration of O$^{2-}$ ions in the barrier layer. Outward migrating Al$^{3+}$ ions are ejected at the pore bases to the electrolyte. Anolyte species are normally incorporated into the films from the electrolyte, e.g. sulfate, phosphate or oxalate ions from sulfuric, 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 absence of fluorine and the absence of zirconium in the present films may be due to the following reactions:

\[
\text{ZrF}_5^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{F}^- + \text{ZrO}_2 + 4\text{HF} \tag{1}
\]

or

\[
\text{ZrF}_5^{2-} \rightarrow \text{ZrF}_n^{(4-n)} + (6 - n)\text{F}^- \tag{2}
\]

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$^+$ ions would migrate away from the film surface.

Alternatively, the following reactions may occur:

\[
\text{ZrF}_5^{2-} + \text{H}^+ \rightarrow \text{ZrF}_3^+ + \text{HF} \tag{3}
\]

\[
\text{ZrF}_5^{2-} + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{ZrOF}^4+ + 4\text{HF} \tag{4}
\]

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.

The absence of zirconium species in the anodic films contrasts with the deposition of zirconium oxide during formation of conversion coatings on aluminium alloys in baths containing fluorozirconic anions. The deposition is favored at cathodic sites on the alloy surface where the pH is locally increased by reduction of oxygen, resulting in the reaction:

\[
\text{ZrF}_5^{2-} + 4\text{OH}^- \rightarrow \text{ZrO}_2 + 2\text{H}_2\text{O} + 6\text{F}^- \tag{5}
\]

On the contrary, during anodizing, the anodic oxidation of the aluminum generates increased acidity according to the reaction:

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

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 IV reveal that the F:Al ratios in films formed in electrolytes containing 3.5 × 10$^{-2}$ and 3.5 × 10$^{-4}$ M sodium fluoride are of a similar order as in films formed in electrolytes containing 0.1 and 1.0 wt% fluorozirconic acid, respectively. However, Table I shows that the concentrations of the fluorooxo and free-fluoride are roughly one and two orders of magnitude lower than the concentrations of the sodium fluoride. This suggests that fluoride ions and/or hydrofluoric acid generated from fluorozirconate ions in Reactions 1 to 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 hexafluoride ions to oxalic acid has a greater influence on film growth than additions of fluoride ions.

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. 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 9. The presence of a fluoride-rich layer at the film base was found by XPS analysis of a film formed in oxalic acid with added fluoride, and is suggested to be present in the films formed in sulfuric acid according to the GDOES profiles of Figure 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 sulfate ions migrate inward more slowly than O$^{2-}$ and fluoride ions, and a region next to the pore/electrolyte interface containing oxide, fluoride and sulfate. A similar cell structure occurs in porous films formed on titanium, and zirconium, 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 fluorooxo ions 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 IV, the concentrations of fluoride ions in the films formed for 300 s in the presence of a fluorooxo at both 0 and 20°C were similar to, or significantly greater than,
the concentration of sulfate ions in the films. Furthermore, comparison with the control specimens showed that the incorporation of fluoride did not significantly influence the incorporation of sulfate. The same applied also to films formed in the presence of sodium fluoride at concentrations of 3.5 × 10⁻³ M and 3.5 × 10⁻¹ M. This behavior contrasts with observations made for barrier type films formed in a range of mixed electrolytes. 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 fluoride 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 sulfuric acid at 20 °C at current densities above 2 mA cm⁻² develop by flow of oxide from the barrier layer into the cell walls. 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 units of AlF₃ into the film. These species may alter the bonding with 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 aluminum of AlF₃ being greater than that of Al₂O₃ 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 II, and the chemical dissolution rates of the films in Table VI, the ratios of the film dissolution rate to growth rates are calculated to be 0.5 × 10⁻³ and 1.2 × 10⁻⁵ for anodizing in the electrolyte containing 0.1 wt% fluorozirconic acid at 0 and 20 °C, respectively, and 1.5 × 10⁻³ and 9.5 × 10⁻⁵ for anodizing in the electrolyte containing 1 wt% fluorozirconic acid 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 and hydrofluoric acid generated from the fluorozirconic acid in Reactions 1 to 4. Thus, the significance of dissolution to the film growth is uncertain from the present results.

Conclusions

1. Additions of fluorozirconic acid or sodium fluoride to sulfuric acid increase the growth rate of anodic films formed on aluminum under a constant voltage of 22 V at 0 and 20 °C. The effect of the fluorozirconic acid 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 fluorooxidic anions and fluoride ions to the base of pores.
3. Increasing the concentration of the fluorooxidic acid or sodium fluoride increases the growth rate. However, film dissolution is also enhanced. This can lead to collapse of the porous structure at the film surface, which is promoted by increased fluorooxidic/fluoride concentration and electrolyte temperature.
4. The films contain oxide, sulfate 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 sulfate ions.
5. The migration rate of fluoride ions is faster than that of sulfate and oxygen ions. Hence, it is expected that a fluoride-rich layer is present at the base of the barrier layer and at the cell boundaries.

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