The development of cerium-rich layers on anodized pure aluminum and AA7075 T6 alloy has been investigated using scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. The surfaces of pure aluminum and AA7075 T6 were pre-treated by alkaline etching and HNO₃ desmutting followed by anodizing in sulfuric acid electrolyte with and without addition of tartaric acid. The outer layer is created by immersion in a cerium (III) nitrate solution containing hydrogen peroxide. It is shown that anodizing in a mixture of sulfuric and tartaric acids prior to the immersion treatment leads to the formation of a thicker and a more uniform cerium-rich layer. The ultramicrotomed sections display the presence of cerium species within the pores of the anodic film. This treatment significantly improves the corrosion resistance of the material.

Recently, sulfuric acid (SA) and tartaric/sulfuric acid (TSA) electrolytes have been used as alternatives to chromic acid for anodizing. However, the use of chromic acid has associated health issues, as well as having a negative environmental impact.

The effect of tartaric acid on the anodic film morphology and corrosion resistance of anodized AA 2024 T3 was studied by Boisier et al. It was found that the addition of tartaric acid to the anodizing electrolyte generates anodic films with reduced porosity and with the pores better distributed over the filmed aluminum surfaces due to the reduced rate of chemical dissolution of the alumina in TSA electrolyte. Several studies have shown that films formed in TSA solution are more resistant to corrosion than films obtained in SA only, but the presence of tartaric acid in the anodizing electrolyte does not change the anodic film morphology.

The protective properties of the anodic oxide films formed in sulfuric acid, with or without tartaric acid, may be enhanced by addition of rare earth compounds (e.g. cerium-based compounds) before, during or after anodizing. The main benefits of cerium-based layers are high corrosion resistance, non-toxicity, and a relatively fast deposition process. Hughes et al., Hinton et al., and Mansfeld et al. achieved enhanced corrosion resistance for AA2024 and 7075 aluminum alloys after spontaneous deposition of conversion coatings in Ce(III) solutions at ambient temperature. Their results have been taken as a starting point for this research. In the present study, a cerium treatment is applied to pure aluminum (99.99 wt%) and AA7075 T6 aluminum alloy after anodizing in order to improve the corrosion resistance provided by the anodic film. This treatment involves immersion of the anodized samples in cerium nitrate solution, which leads to deposition of cerium oxide/hydroxides on the surface and within the pores of the film. Additionally, the effect of tartaric acid on the morphology and the chemical composition of the cerium-rich layer formed as a result of the immersion treatment has been investigated.

Aluminum alloys are widely used in the aerospace industry because of their high strength to weight ratio. The high strength is achieved by alloying with copper, magnesium, silicon, manganese, and zinc. However, the resulting microstructure contains intermetallic particles that are more or less noble than the alloy matrix, thereby increasing the corrosion susceptibility of the alloy compared with high purity aluminum. Traditionally, anodizing in chromic acid electrolyte has been used for corrosion protection, with the presence of residual chromate ions within the pores of the anodic film providing corrosion inhibition. However, the use of chromic acid has associated health issues, as well as having a negative environmental impact.

Recently, sulfuric acid (SA) and tartaric/sulfuric acid (TSA) electrolytes have been used as alternatives to chromic acid for anodizing. However, the use of chromic acid has associated health issues, as well as having a negative environmental impact.

The experimental setup involved immersion of the anodized samples in cerium nitrate solution, which leads to deposition of cerium oxide/hydroxides on the surface and within the pores of the film. Additionally, the effect of tartaric acid on the morphology and the chemical composition of the cerium-rich layer formed as a result of the immersion treatment has been investigated.
In order to highlight the morphology of the coating, scanning transmission electron microscopy (STEM), employing high angle annular dark field (HAADF) imaging, was used in the Tecnai F30 instrument. The electron microscopes were equipped with energy dispersive X-ray (EDX) spectroscopy facilities for qualitative and quantitative elemental analyses. X-ray photoelectron spectroscopy (XPS) was employed, using a Kratos Axis Ultra DLD XPS spectrometer with a monochromated Al K$_\alpha$ source (1486.6 eV), to determine the surface composition of the protective cerium-containing layers and the valence of the cerium species present in the layer. The operating pressure was less than $2 \times 10^{-5}$ Pa and the analysis area was $700 \times 300 \mu$m$^2$. Surface elemental concentrations were determined by measuring the photoelectron peak areas and using Scofield$^{20}$ sensitivity factors, taking into account the intensity/energy response of the instrument.$^{21}$ High energy resolution spectra were acquired for chemical state determination, and charge corrected by reference to the C1s hydrocarbon peak at 285 eV. Monte Carlo error analysis was undertaken for the Ce 3d peak fitted components in order to determine the significance of small changes in chemistry. All processing was carried out using CasaXPS version 2.3.17 (Casa Software, Teignmouth, UK).

Results and Discussion

Characteristics of the cerium-rich protective layers. — Surface characteristics.— Scanning electron micrographs of the specimens after anodizing and cerium post-treatment are presented in Figure 1, where it is evident that the cerium-rich layers consist of approximately spherical particles. The layer formed on the anodic film obtained in SA solution on pure aluminum (Fig. 1a) is not uniformly distributed over the anodized surface and displays relatively little coverage on some regions. The typical size of the particles is in the range of 10–15 nm. Conversely, the layer formed on pure aluminum during cerium post-treatment after TSA anodizing is more uniform, and consists of larger particles (20–25 nm) that are clearly revealed in the micrograph (Fig. 1b). The cerium-based layers formed on the anodized AA7075 T6 alloy were also less uniform after SA anodizing compared with the coating developed after TSA anodizing (Fig. 1c, 1d). The characteristic dimensions of the Ce-rich particles were in the range of 10–15 nm (Fig. 1c) after anodizing in SA and 10–20 nm after anodizing in TSA (Fig. 1d). In the latter case, it is difficult to distinguish individual particles since they have merged to form agglomerates that have resulted in the formation of an apparently continuous film over the anodized surface. The film displays some cracks at the boundaries of the cerium agglomerates, with widths up to 100 nm (Fig. 1d). The presence of these cracks on the cerium layer may indicate dehydration and shrinkage as a result of drying of the coating, or further dehydration in the SEM vacuum chamber.

For both pure aluminum and the AA7075 T6 alloy, the post-treated surfaces of the specimens after SA anodizing are pale yellow, whereas, after TSA anodizing and cerium post-treatment, the surface displays an intense yellow color. The increased intensity of the yellow color may indicate an increased thickness of the cerium-rich layer. However, a further reason for the intense yellow color may be an increased presence of Ce$^{3+}$ compounds. More detailed measurements of Ce$^{3+}$ and Ce$^{4+}$ species are presented later using XPS analysis.

Cross-sections of the cerium-rich layers.—Transmission electron micrographs of ultramicrotomed sections revealed the detailed morphologies of the cerium-rich layers on pure aluminum (Figs. 2, 3 and 4). From the micrographs, it is evident that the treatments applied to the metal substrates lead to the presence of a double-layer film, comprising a relatively thick porous anodic alumina layer (0.94 μm and 0.97 μm after anodizing in SA and TSA respectively) below a relatively thin cerium-rich layer. The thicknesses of the cerium oxide/hydroxide layers formed after anodizing in SA and TSA electrolytes are in the region of 50–60 nm and 80–90 nm respectively (Fig. 2a, 2b).

The transmission electron micrographs also reveal the presence of cerium-containing particles within the pores of the anodic film (confirmed by EDX analysis). Comparison between Fig. 2a and 2b indicates that the addition of tartaric acid to the anodizing bath prior to the cerium treatment results in an increase of the thickness of the Ce-rich film as well as promoting the deposition of cerium species.
within the pores of the anodic layer. This difference is confirmed by examination of the HAADF images of Figs. 3a, 3b. Cerium containing layers (generally cerium conversion coatings) may have amorphous or crystalline structure, depending on the deposition parameters.\textsuperscript{11,22,23} In order to evaluate the structure of the cerium-rich film on anodized pure aluminum presented here, the outer layer was assessed by high resolution BF (bright field) imaging and diffraction patterns were obtained by Fast Fourier transforms (FFT) as displayed in Fig. 4a, 4b respectively. The d-spacings measured for cerium oxide layers on pure aluminum confirm the formation of CeO\textsubscript{2}, on the surface with (111), (200), (220) and (311) reflections of the fcc structure, which has a characteristic lattice parameter of $a=0.541$ nm.\textsuperscript{24}

**Chemical analysis.**—In order to determine the cerium concentrations in the different specimens, EDX analysis was employed (points O1 and O2 in Fig. 3). Measurements of the cerium and oxygen concentrations are shown in Table I for pure aluminum anodized in SA and TSA electrolytes respectively. It is evident that the cerium-rich layer on the sample anodized in SA contains about 32–37 at.% of cerium and 62–65 at.% of oxygen compared to 31–32 at.% of cerium and 67–68 at.% of oxygen for the sample anodized in TSA.

XPS was undertaken in order to establish the relative abundances of the different compounds in the Ce-rich layers generated on the anodized aluminum surfaces. A typical wide range survey spectrum is shown in Fig. 5, which indicates the presence of cerium, aluminum, oxygen, sulfur and carbon. The last is present due to contamination from the environment. Table II shows the elemental atomic concentrations. Samples of AA7075 T6 alloy after anodizing in TSA and pure aluminum samples after SA and TSA show similar surface elemental concentrations of cerium, between 8.5 at.% and 10.3 at.%, whereas the AA7075 T6 alloy sample after anodizing in SA shows only 1.8 at.%. Addition of tartaric acid to the anodizing electrolyte results in higher Ce concentrations, due to the deposition of a thicker cerium-rich layer. The sample of AA7075 T6 alloy after anodizing in SA and cerium-based treatment also shows higher concentrations of aluminum and oxygen on the surface, and lower concentrations of sulfur and carbon, suggesting dissolution of the surface may be occurring. Oxygen is associated with aluminum, since the surface shows the anodic film with cerium precipitates (Fig. 1c).

Inspection of the Ce 3d photoelectron region shows a complex of overlapping peaks originating from Ce\textsuperscript{3+} and Ce\textsuperscript{4+} species. Ten peaks are required to fit the spectrum due to spin orbit splitting and final state effects.\textsuperscript{26} The results are shown for the pure aluminum and AA7075 T6 alloy samples in Figs. 6 and 7 respectively. All peaks have a Gaussian (70%) Lorentzian (30%) product shape and spin orbit component intensities in the ratio 3:2.

Following peak fitting, the Ce\textsuperscript{3+}/Ce\textsuperscript{4+} concentration ratio and error estimate have been determined (Table III). The Table reveals that the only significant concentration ratio difference is for the AA7075 T6 alloy sample after anodizing in SA followed by cerium-based treatment with a value of 3.25 compared with values between 2.23 and 2.45 for the other samples. It can be seen that measurements for pure aluminum strongly indicate a slight decrease in the abundances of Ce\textsuperscript{4+} after anodizing in TSA electrolyte. Thus, the Ce\textsuperscript{3+}/Ce\textsuperscript{4+} ratio in pure aluminum anodized in TSA is about 10% lower than that after anodizing in SA. This ratio is further reduced for the AA7075 T6 alloy anodized in TSA, being about 30% lower than that of the sample anodized in SA.

Figures 8 and 9 show the results of peak fitting to the O1s photoelectron region. The peaks at 529.3 eV and 530.0 eV are assigned as oxide and hydroxide bonded to cerium respectively. The peaks at 531.3 eV and 532.2 eV are assigned as oxide and hydroxide bonded to cerium respectively. The peaks at 529.3 eV and 530.0 eV are assigned as oxide and hydroxide bonded to cerium respectively. The peaks at 531.3 eV and 532.2 eV are assigned as oxide and hydroxide bonded to cerium respectively. The remaining two peaks at higher binding energies, 533.5 eV and 535.3 eV, are considered to originate from environmental contamination.\textsuperscript{27,28}

Comparison of Figs. 8a, 8b and 9a, 9b also indicate that the addition of tartaric acid resulted in a higher concentration of cerium oxides and hydroxides. The intensities of the peaks associated with aluminum oxide and hydroxide in Fig. 9a are comparatively higher.

### Table I. EDX abundances of elements in the cerium-rich layer formed after anodizing of pure aluminum in SA and TSA electrolytes.

| Elements, at.% | SA | TSA |
|---------------|----|-----|
| O (K)         | 62.17 | 65.98 |
| Al (K)        | 0.12 | 1.74 |
| Ce (L)        | 37.71 | 32.28 |

### Table II. Elemental concentrations determined by XPS.

| Specimens | Ce (% at.) | S (% at.) | Al (% at.) | O (% at.) | C (% at.) | Std Dev |
|-----------|------------|-----------|------------|-----------|-----------|---------|
| A SA      | 8.5        | 2.2       | 2.5        | 33.4      | 53.4      | 0.09    |
| A TSA     | 9.2        | 2.5       | 0.6        | 33.9      | 53.9      | 0.08    |
| AA7075 SA | 1.8        | 0.2       | 16.9       | 46.5      | 34.7      | 0.11    |
| AA7075 TSA| 10.3       | 2.7       | 0.6        | 33.6      | 52.8      | 0.07    |
Figure 6. The high resolution Ce3d XPS spectrum around the binding energy of 900 eV for the pure aluminum anodized in SA (a) and TSA (b). The black solid line is the experimental XPS spectrum of the sample. Other lines correspond to Gaussian approximations for different Ce$^{3+}$ and Ce$^{4+}$ photoelectron lines providing the best fit for the observed spectrum. Binding energies for each component are shown on the plot.

Figure 7. The high resolution Ce3d XPS spectrum around the binding energy of 900 eV for the AA7075 T6 alloy anodized in SA (a) and TSA (b).

| Specimens | Ce$^{4+}$/Ce$^{3+}$ ratio | Ce OH$^{-}$/O$_2^-$ | Al OH$^{-}$/O$_2^-$ | Std Dev |
|-----------|-----------------|-----------------|-----------------|---------|
| A SA      | 2.45            | 0.55            | 0.54            | 0.09    |
| A TSA     | 2.23            | 0.29            | 0.50            | 0.08    |
| AA7075 SA | 3.25            | 3.07            | 1.06            | 0.11    |
| AA7075 TSA| 2.23            | 0.80            | 0.71            | 0.07    |

Table III shows the hydroxide/oxide ratios for aluminum and cerium. Significantly different values of this ratio are seen for aluminum and cerium in the AA7075 T6 alloy after anodizing in SA and Ce-based post-treatment than for the other three samples.

Mechanism of the formation of cerium-rich layer.—The formation of a cerium-rich layer on the anodic film involves several chemical reactions. Cerium can be precipitated due to an increase of the pH value on the interface between the anodic oxide film and the post-treatment solution. The first step is the dissolution of the anodic alumina film in the cerium-based solution (pH 3.75):

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

Figure 8. The high resolution O1s XPS spectrum around the binding energy of 530 eV for the pure aluminum anodized in SA (a) and TSA (b).
Figure 9. The high resolution O1s XPS spectrum around the binding energy of 530 eV for the AA7075 T6 alloy anodized in SA (a) and TSA (b).

The second step is the precipitation of cerium on the surface of the anodic film and within the pores due to the local rise in pH. Hydrogen peroxide present in the solution plays an important role in transforming Ce$^{3+}$ to Ce$^{4+}$ at pH $>2$. Oxidation of Ce$^{3+}$ to Ce$^{4+}$ by H$_2$O$_2$ occurs also when the pH increases. This process changes the color of the solution from colorless to yellow, according to 15,29. Increase of the pH value contributes to precipitation of cerium oxides through 2 pathways. The first pathway is through Ce(III), present in the initial Ce(III) nitrate solution (Eq. 2, 3), and the second pathway is through Ce(IV) species (Eq. 4–7).29 The latter is possible only in the presence of H$_2$O$_2$. Concerning the Ce(III) pathway, the precipitation of cerium products is described by the following reactions:

$$Ce^{3+} + 3\text{OH}^- \rightarrow Ce(OH)_3 \quad [2]$$

$$2\text{Ce(OH)}_3 \rightarrow \text{Ce}_2\text{O}_3 + 3\text{H}_2\text{O} \quad [3]$$

Concerning the Ce(IV) pathway, initial oxidation of Ce(III) takes place in the hydrogen peroxide-containing solution (at pH above 2).

$$2\text{Ce}^{3+} + 2\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow 2\text{Ce(OH)}_2^{2+} \quad [4]$$

Subsequently, for pH values between 2 and 5:

$$\text{Ce(OH)}_2^{2+} + 2\text{OH}^- \rightarrow \text{Ce(OH)}_4 \rightarrow \text{CeO}_2 + 2\text{H}_2\text{O}. \quad [5]$$

Also, other reactions in H$_2$O$_2$-assisted solutions are possible, where Ce$^{3+}$ ions can be directly oxidized to Ce(IV) species without intermediate Ce(OH)$_3^{2+}$ by the following reactions:

$$2\text{Ce}^{3+} + 6\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow 2\text{Ce(OH)}_4 \quad [6]$$

$$2\text{Ce}^{3+} + 6\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow 2\text{CeO}_2 + 4\text{H}_2\text{O} \quad [7]$$

These reactions show that the oxidation of Ce$^{3+}$ to Ce(OH)$_4$ occurs through intermediate species, such as Ce(OH)$_3^{2+}$ at pH $<2$ and Ce(OH)$_2^{2+}$ at pH $>2$, according to the E-pH diagrams of the Ce - H$_2$O - H$_2$O$_2$ system, presented in 29. Thus, Ce(IV) can exist in several species, such as Ce(OH)$_3^{2+}$, Ce(OH)$_2^{2+}$ and Ce(OH)$_4$.

According to XPS results, the concentration of Ce$^{3+}$ is higher for samples anodized in TSA followed by cerium-based post-treatment. It is likely that the addition of tartaric acid to the anodizing electrolyte decreases the chemical dissolution rate of the alumina oxide film in the acidic environment.30 Thus, the local pH near the interface between the alumina and post-treatment solution remains lower compared to the pH in proximity of the oxides generated in the absence of tartaric acid. This could result in increased Ce$^{3+}$.31

Corrosion test results.—The corrosion behavior of the anodized AA7075 T6 alloy with a cerium-rich layer has been studied by immersion in naturally aerated 3.5% NaCl solution for 96 h. After immersion, the surfaces were examined using optical and scanning electron microscopes. Six specimens have been examined for each case, with the typical surface appearances shown in Figs. 10 and 11 for the AA7075 alloy specimens treated in SA and TSA after cerium post-treatment respectively. For the specimens that have not been subsequently treated in the cerium-based solution, substantial corrosion (degradation) is revealed.
In both cases, around 70-80% of the anodic alumina is lost (dark areas in Figs. 10a and 11a). Conversely, the anodic layers on the specimens treated in cerium-based solution are mostly unaffected, although some pits and cavities are evident (Figs. 10b and 11b). Analysis of specimens anodized in SA shows that the anodic alumina was removed from around 11% of the surface, while specimens anodized in TSA lost only 3-4% of their surface.

Pits are uniformly distributed on the specimen surfaces. The scanning electron micrograph of a specimen anodized in SA shows that the typical depth of the pits is around 2-2.5 μm. Interestingly, the cavities on the surfaces of specimens anodized in TSA are much shallower (50-60 nm) (Fig. 11c). These cavities are distributed on the cerium-rich layer and do not affect the anodic alumina and substrate beneath it. Further discussion of corrosion of specimens after anodizing in SA/TSA electrolytes and post-treatment in cerium-based solution will be provided in a later paper, based on potentiodynamic polarization and electrochemical noise analysis results.

Summary

This study focused on the formation of cerium-based layers to improve the corrosion resistance of anodized pure aluminum and AA7075 T6 alloy. It is shown that it is possible to obtain a cerium-containing layer with a typical thickness of 50-100 nm after immersion for 30 min. The layer contains mainly Ce(III) and Ce(IV) oxides and hydroxides. The morphology of the layer depends significantly on the composition of the electrolyte used for anodizing. Thus, addition of tartaric acid to the anodizing electrolyte leads to a significant enhancement in the thickness of the cerium-containing layer, as well as to an improvement in its uniformity over the surface of the anodic film. Further, the samples anodized in the presence of tartaric acid display cerium oxide particles within the pores of the anodic film. As a result, the specimens anodized in the mixture of sulfuric and tartaric acids demonstrate noticeably improved corrosion resistance compared with specimens anodized only in sulfuric acid. The results suggest that, for corrosion resistance, the increased thickness and more uniform distribution of the protective layer are more important than the relative abundances of Ce(III) and Ce(IV). The influence of tartaric acid addition to the anodizing electrolyte is not clear yet. This requires further study.

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