Surface pre-treatment of aluminum alloys is important for improvement in the properties and the anticorrosion performance of anodic films and conversion coatings used in the aerospace industry. The main purpose of the pre-treatment is to prepare a reproducible, chemically active surface for application of the subsequent treatment. The pre-treatment of the alloys involves several steps, including degreasing, acid or alkaline etching and desmutting.

Enhanced mechanical properties of the alloys are achieved by addition of alloying elements that form second phase particles. The presence of cathodically active intermetallics on the alloy surface sustains cathodic reactions that cause susceptibility to corrosion due to microgalvanic coupling between the intermetallics and the aluminum matrix and the associated alkaline corrosion. Porous anodic films formed on Al-Cu alloys are less regular than films produced on high purity aluminum due to the incorporation of copper into the film and oxygen evolution during anodizing. Furthermore, the anodic layer formed on the intermetallic particles has an altered morphology and contains various defects, thus providing reduced corrosion protection compared with the aluminum matrix.

For the last two decades, rare earth metals (cerium, neodymium and lanthanum) have been investigated in surface treatments for enhancing the corrosion resistance of anodized aluminum alloys. The treatments can reduce the number of residual cathodic intermetallic particles on the alloy surface and hence enable formation of an anodic film that contains fewer defects. In this regard, relatively little information about cerium-containing desmutting solutions has been published.

Experimental

2024 T3 aluminum alloy (nominal composition in wt%: Cu 3.8-4.9; Mg 1.2-1.8; Mn 0.3-0.9; Zn < 0.25; Fe < 0.5; Cr < 0.1; Si < 0.5; Ti < 0.15; Al bal.) was employed in this research. Specimens of dimensions of 33 × 15 mm were cut with a guillotine from the 0.8 mm thick sheet, then degreased in acetone and ethanol, dried in a cool air stream and etched for 30 s in 10 wt% NaOH solution at 60°C followed by desmutting at ambient temperature using one of the following methods: i) 1.37 M HNO₃ for 30 and 60 s, ii) 1.37 M HNO₃ + 0.013 M CeCl₃ for 30 and 60 s or iii) 1.37 M HNO₃ + 0.013 M CeCl₃ + 0.029 M H₂O₂ for 3, 6 and 9 min. All chemicals were provided by Fisher Scientific UK Ltd. Based on the concentration of HNO₃, the pH of the base solution was in the range of −0.14, and it is unlikely that the low levels of CeCl₃ and H₂O₂ additions resulted in significant differences in pH values. The etching and desmutting processes were followed by rinsing in deionized water and drying in a cool air stream.

Prior to potentiodynamic polarization tests and anodizing, the individual specimens were examined by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX), using a Carl Zeiss Ultra 55 instrument at accelerating voltages of 1.5 and 15 keV, respectively, in order to determine their chemical compositions and surface morphologies. EDX analysis was performed at an accelerating voltage of 15 keV. Intermetallic particles on alloy before etching and desmutting were observed by SEM using block specimens prepared using ultramicrotomy with a diamond knife using a Leica Ultracut Instrument.

Potentiodynamic polarization tests were carried out in naturally aerated 3.5 wt% NaCl solution at ambient temperature using a three-electrode cell with a Solartron SI 1287 potentiostat. The alloy specimens, with an exposed area of 1 cm², a platinum electrode and a saturated calomel electrode (SCE) were used as the working electrode, the counter electrode and the reference electrode, respectively. The potential was varied between −0.03 V vs. the open circuit potential (OCP) and −0.2 V vs. the SCE for anodic polarization, and between 0.03 V vs. OCP and −1.8 V vs. SCE for cathodic polarization. A scan rate of 0.16 mV/s was employed.

Potentiodynamic anodizing was undertaken in stirred 0.46 M H₂SO₄ electrolyte at ambient temperature using a similar three-electrode cell with the potential scan performed from 0 V vs. OCP to 14 V vs. SCE at 16.66 mV/s, with an exposed specimen area of 1 cm². The surface composition was investigated using a Kratos Axis Ultra DLD XPS spectrometer with a monochromated Al Kα source (1486.6 eV). The operating pressure was less than 2 × 10⁻⁶ Pa and the analysis area was 700 × 300 μm². The Cl₁s hydrocarbon peak (285.0 eV) was used for calibration of the binding energies. Individual specimens of area of approximately 0.25 cm² were mounted on a stainless steel holder using double sided adhesive tape.

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Al-Mn dispersoids (labeled 4), and the irregularly-shaped Al-Cu-Fe-Mn-(Si) particles (labeled 3, 6) and the internal parts of the particles are enriched with Fe or Mn (labeled 7, 8 and 9, 10 respectively). The differing brightness of the internal and external parts of Al-Cu-Fe-Mn-(Si) particles in the backscattered electron image suggests a non-uniform distribution of elements within the particles. EDX analysis identified an enrichment of iron and manganese in the internal part of the particles (Table I) that was possibly generated during the early stages of solidification. Small particles with different concentrations of Fe and Mn within larger Al-Cu-Fe-Mn-(Si) intermetallics were observed in earlier work. The formation of relatively small size, individual Al-Cu-Fe-Mn-(Si)-containing particles grouped in clusters can be explained by the low solubility of Fe and Mn in the aluminum matrix.

After etching in sodium hydroxide solution and desmutting for 30 or 60 s in nitric acid, the surface revealed a scalloped appearance with removed, partly dissolved and whole intermetallic particles present in cavities with trenching around them (Figs. 3a and 3b). After 30 s the surface has a scalloped appearance due to the progressive de-alloying. The alloy matrix around intermetallics is dissolved resulting in undermining and loss of smaller particles. However, larger intermetallic particles remain for short times of desmutting.

In contrast to desmutting in nitric acid alone, no S, 0-phases and Al-Cu-Fe-Mn-(Si) particles were observed on the surface after desmutting 30 and 60 s with addition of CeCl₃ (Figs. 3c and 3d). The surface revealed scalloping of similar shape and size as the intermetallic particles, which had been removed by dissolution and detachment. Only a small amount of copper (1.6-2.0 at.%) was left on the surface compared with specimens treated in nitric acid only (16.25 at.%). A longer time of desmutting resulted in dissolution of aluminum at the periphery of the Al-Cu-Fe-Mn-(Si) particles (Fig. 3d).

The micrographs of specimens desmutted in the solution with 

\[
\begin{align*}
    d_{Al} &= \frac{\lambda_{Al}}{\cos \Theta} \times \ln \left( 1 + \frac{I_{Al}^{3+} I_{Al}^{0}}{I_{Al}^{0} I_{Al}^{3+}} \right),
\end{align*}
\]

where \( \Theta \) is the photoemission angle (angle of detection), \( \lambda_{Al} \) is the mean free path of electrons with kinetic energy corresponding to the Al2p photoelectron line, \( I_{Al}^{3+} \) and \( I_{Al}^{0} \) are the intensities of the oxidized and metal components obtained after fitting of the Al2p peak, and \( I_{Al}^{0} \) and \( I_{Al}^{3+} \) are the intensities obtained from the pure aluminum. The variation in values of thickness is considered real and confidence in the values arises from repeated measurements for each condition. All data processing was carried out using CasaXPS version 2.3.17 (Casa Software, Teignmouth, UK). For each surface treatment, 10 specimens were produced under nominally identical conditions and the analysis presented was performed on at least three different specimens produced under nominally identical conditions for reproducibility; the average behavior is presented.

Results and Discussion

Surface characteristics.—Initially, the morphology and composition of the intermetallic particles (IMCs) in the 2024 T3 aluminum alloy were characterized by SEM/EDX. The distributions of the particles on the ultramicrotomed block specimen of the as-received alloy are shown in Fig. 1. Four types of intermetallic particle were present. The micrographs in Fig. 1 reveal round-shaped Al-Cu-Mg (S-phase) particles (labeled 1 and 2), Al-Cu (0-phase) particles (labeled 3), Al-Mn dispersoids (labeled 4), and the irregularly-shaped Al-Cu-Fe-Mn-(Si) IMCs (labeled 5-10). The respective particles have typical sizes in the ranges of 1-5 μm, 0.5-1 μm and 2-8 μm. These particles have been characterized in many previous studies. Table I shows the elemental atomic concentrations detected by EDX analysis. The Mg/Cu ratio helps to distinguish the 0 and S-phases. The ratio for respective particles are in the region of 0.22-0.27 and 0.78-0.90. The magnesium detected at locations of the 0-phase particles originates from the underlying matrix.

A cluster Al-Cu-Fe-Mn-(Si) particle is shown in Fig. 1b. In some of the Al-Cu-Fe-Mn-(Si) particles no silicon was detected (labeled 5 and 6) and the internal parts of the particles are enriched with Fe or Fe and Mn (labeled 7, 8 and 9, 10 respectively). The differing brightness of the internal and external parts of Al-Cu-Fe-Mn-(Si) particles in the backscattered electron image suggests a non-uniform distribution of elements within the particles. EDX analysis identified an enrichment of iron and manganese in the internal part of the particles (Table I) that was possibly generated during the early stages of solidification. Small particles with different concentrations of Fe and Mn within larger Al-Cu-Fe-Mn-(Si) intermetallics were observed in earlier work. The formation of relatively small size, individual Al-Cu-Fe-Mn-(Si)-containing particles grouped in clusters can be explained by the low solubility of Fe and Mn in the aluminum matrix.

Table I. The elemental atomic concentrations of intermetallic particles of the AA2024 T3 before pre-treatment determined by EDX analysis (% at.).

| IMCs | Mg | Al | Mn | Si | Fe | Cu |
|------|----|----|----|----|----|----|
| 1 | 15.1 | 63.6 | - | - | - | 19.3 |
| 2 | 18.9 | 60.4 | - | - | - | 20.8 |
| 3 | 0.6 | 78.5 | - | - | - | 19.9 |
| 4 | 0.8 | 87.5 | - | - | - | 11.7 |
| 5 | 1.3 | 86.4 | 2.1 | - | 2.1 | 8.1 |
| 6 | 0.9 | 85.4 | 3.1 | - | 1.9 | 8.7 |
| 7 | 0.8 | 74.8 | 2.5 | 0.2 | 4.7 | 17.0 |
| 8 | 0.4 | 72.0 | 3.2 | 0.9 | 6.7 | 16.9 |
| 9 | 0.1 | 71.3 | 7.5 | 4.7 | 8.5 | 7.8 |
| 10 | 0.2 | 71.8 | 7.3 | 4.8 | 8.1 | 7.8 |

Figure 1. Backscattered electron micrographs of ultramicrotomed sections of the as-received 2024 T3 aluminum alloy (a,b).

The micrographs of specimens desmutted in the solution with CeCl₃ and H₂O₂ additions for 3, 6 and 9 min show features on the surface similar to those resulting from treatment with added CeCl₃ (Figs. 2a and 2b). The surface revealed scalloping of similar shape and size as the intermetallic particles, which had been removed by dissolution and detachment. Only a small amount of copper (1.6-2.0 at.%) was left on the surface compared with specimens treated in nitric acid only (16.25 at.%). A longer time of desmutting resulted in dissolution of aluminum at the periphery of the Al-Cu-Fe-Mn-(Si) particles (Fig. 2d).

The micrographs of specimens desmutted in the solution with CeCl₃ and H₂O₂ additions for 3, 6 and 9 min show features on the surface similar to those resulting from treatment with added CeCl₃ only (Figs. 3a-3c). After 3 min, the surface has a scalloped appearance with partly removed and dissolved Al-Cu-Mg, Al-Cu-Fe-Mn and Al-Mn particles and precipitated copper oxide particles (Fig. 3a). It is difficult to distinguish the size of the individual copper oxide particles due to their agglomeration. After 6 min, more S-phase particles were removed and no Al-Cu-Fe-Mn-(Si)-containing particles were detected (Fig. 3b). Some partly dissolved Al-Cu-Mg particles were covered by copper oxide particles. After 9 min, no intermetallic particles were observed (Fig. 3c). According to EDX analysis, the copper concentration decreased significantly with time, with concentrations of 18-32, 19.2-5.2 and 1.7-1.9 at.%, respectively. More detailed measurements of the Cu species are presented later using XPS analysis. The slower removal of intermetallic particles in the presence of H₂O₂ is possibly...
Figure 2. Scanning electron micrographs of the 2024 T3 aluminum alloy after etching followed by desmutting in 1.37 M HNO₃ (a,b) and 1.37 M HNO₃ + 0.013 M CeCl₃ (c,d), treated for 30 s (a,c) and 60 s (b,d). Areas of interest shown at higher magnification are inset into the micrographs (white dashed rectangles).

due to a local increase in the pH that slows the dissolution of oxide covering the particles.

Optical micrographs show that in the presence of CeCl₃, grain boundary attack is significantly reduced. Figs. 4a and 4b compare specimens after desmutting in the absence and in the presence of CeCl₃, respectively; arrows indicate the grain boundaries that were attacked. Clearly, the number of the grain boundaries attacked and the extent of the attack was higher for the specimens desmutted in the absence of CeCl₃.

Additional desmutting experiments were undertaken in order to distinguish the effects from Ce³⁺ and Cl⁻ ions using two solutions with different sources of Ce³⁺ and Cl⁻. Fig. 5a shows that S-phase particles were absent from the surface after desmutting for 30 s in 1.37 M HNO₃ + 0.013 M Ce(NO₃)₃ while in Al-Cu-Fe-Mn-(Si) particles EDX analysis revealed preferential dissolution of Al, Fe and Mn. Conversely, desmutting for 30 s with the addition of 0.039 M NaCl to the nitric acid resulted in removal of Al-Cu-Fe-Mn-(Si) particles and dealloying of S-phase particles, leaving a copper-rich sponge (Fig. 5b). In the absence of cerium, de-alloyed S-phase remained on the surface following desmutting in nitric acid alone and also with addition of NaCl. In contrast, residual S-phase was not detected when CeCl₃ or Ce(NO₃)₃ were added, suggesting that the cerium accelerates the removal of the residues irrespective of the presence of Cl⁻ ions. In contrast, Cl⁻ ions appear to accelerate the removal of Al-Cu-Fe-Mn-(Si) particles, which were not detected following desmutting in solutions containing NaCl or CeCl₃. The presence of copper in the alloys increases the attack by Cl⁻ ions due to the formation of oxyhalide complexes that may cause the natural passivity to decrease.
Figure 4. Optical micrographs of 2024 T3 after etching followed by desmutting for 30 s in 1.37 M HNO₃ (a) and 1.37 M HNO₃ + 0.013 M CeCl₃ (b).

Chemical analysis.—XPS was undertaken in order to determine the concentration of different species on the surface after pre-treatment for different times in HNO₃ + CeCl₃ or HNO₃ + CeCl₃ + H₂O₂. Typical wide range spectra are shown in Figs. 6a–6d, indicating the presence of aluminum, oxygen, carbon, nitrogen, copper, magnesium, iron, manganese and chlorine (Table II). Carbon is present as a contaminant from the environment. As shown below, the oxide films on the alloy surface were 4 nm thick. Since the depth of the XPS analysis was about 5 to 10 nm, elements present in the substrate may be detected. No significant change in the element concentrations was observed with increasing time of treatment in either HNO₃ or HNO₃ + CeCl₃ solutions. A low concentration of chlorine was detected on the surface of the alloy treated in the CeCl₃-containing solution. The concentrations of Cl⁻ ions after desmutting for 30 and 60 s with addition of CeCl₃ were 0.5 and 1.5 at.% respectively, and 0.6, 0.9 and 1.5 at.% after desmutting for 3.6, and 9 min, respectively with additions of CeCl₃ and H₂O₂ (Table II).

Due to the Al2p and Cu3p peaks overlapping, the real concentrations of elements can only be obtained by peak fitting. Figs. 7a and 7b display the results of peak fitting of the Al2p high resolution spectra. The following four components were found: i) two metallic Al peaks (Al2p₃/₂ and Al2p₁/₂) at 71.9 and 72.3 eV, respectively, ii) oxidized

| Sample                      | Al2p + Cu3p | O1s | Cu2p₃/₂ | N1s | Ca2p | Na1s | Cl2p | Cl1s |
|-----------------------------|-------------|-----|---------|-----|------|------|------|------|
| 30 s HNO₃                   | 28.1        | 40.0| 0.5     | 0.4 | 0.2  | 0.0  | -    | 30.7 |
| 60 s HNO₃                   | 31.6        | 35.5| 0.9     | 0.5 | 0.4  | 0.1  | -    | 31.1 |
| 30 s HNO₃ + CeCl₃           | 27.9        | 35.7| 0.2     | 0.5 | 1.0  | 0.4  | 0.5  | 33.8 |
| 60 s HNO₃ + CeCl₃           | 29.3        | 34.0| 0.8     | 0.5 | 0.2  | 0.0  | 1.5  | 33.7 |
| 3 min HNO₃ + CeCl₃ + H₂O₂   | 26.9        | 37.5| 0.6     | 0.8 | 0.6  | 0.0  | 0.6  | 33.1 |
| 6 min HNO₃ + CeCl₃ + H₂O₂   | 26.1        | 34.8| 0.4     | 0.7 | 0.5  | 0.0  | 0.9  | 36.6 |
| 9 min HNO₃ + CeCl₃ + H₂O₂   | 29.4        | 31.9| 0.9     | 0.9 | 0.3  | 0.0  | 1.5  | 35.2 |

Figure 5. Scanning electron micrographs of the 2024 T3 aluminum alloy after etching followed by desmutting for 30 s in (a) 1.37 M HNO₃ + 0.013 M Ce(NO₃)₃ and (b) 1.37 M HNO₃ + 0.039 M NaCl.

Figure 6. Typical wide range survey XPS spectra of the AA2024 T3 after etching followed by desmutting in 1.37 M HNO₃ (a,b) and 1.37 M HNO₃ + 0.013 M CeCl₃ (c,d), treated for 30 s (a,c) and 60 s (b,d).
Figure 7. The high resolution Al2p spectra of AA2024 T3 after etching followed by desmutting for 30 s in 1.37 M HNO3 (a) and 1.37 M HNO3 + 0.013 M CeCl3 (b).

Figure 8. The high resolution Cu2p spectra of AA2024 T3 after etching followed by desmutting for 30 s in 1.37 M HNO3 (a) and 1.37 M HNO3 + 0.013 M CeCl3 (b).

Corrosion behavior.—Potentiodynamic polarization curves for the variously pre-treated specimens were obtained after OCP measurements for 15 min (Figs. 9a, 9b). The corrosion potentials (Ecorr) are slightly higher for samples treated in HNO3 + CeCl3 and HNO3 + CeCl3 + H2O2 (−0.56 and −0.57 V vs. SCE, respectively), than for nitric acid only (−0.6 V vs. SCE), probably due to a decreased anodic activity. Comparison of the polarization curves for the specimens reveals a reduced current density with the cerium-containing solution at small cathodic polarizations. In this region, oxygen reduction occurs under activation control mainly on large intermetallic particles. Thus, a reduced number of the particles results in a reduced

metal (Al3+) AlOx2p3/2 and AlOx2p1/2 at 74.3 and 74.7 eV, respectively, and iii) Cu3p1/2 and Cu3p3/2 at 75.2 and 77.5 eV, respectively (Fig. 7). The alloy surface was covered with aluminum oxide after removing the smut layer formed during etching in sodium hydroxide solution. The thickness of the oxide layer was determined using eq. 1. After desmutting in nitric acid only for 30 and 60 s, the film thicknesses were 4.4 and 4.0 (±0.1) nm, respectively, while in the presence of CeCl3, the respective values were 4.1 and 3.6 (±0.1) nm. The thickness of the aluminum oxide layer formed after desmutting in HNO3 is in good agreement with the results presented in the literature.28 The thicknesses of the aluminum oxide layer after desmutting in HNO3 + CeCl3 + H2O2 solution for 3, 6, 9 min were 4.8, 3.9, 3.6 (±0.1) nm, respectively. The findings suggest a small reduction in thickness with increased desmutting time for all solutions.

Fitting of the Cu2p3/2 peaks was undertaken to determine the oxidation state of copper present on the alloy surface after desmutting (Figs. 8a, 8b). The peaks revealed the presence of Cu0 (metal) and Cu+ (Cu2O) species with binding energies of 932.6 and 932.2 eV, respectively. Their presence was also identified using the Auger electron peaks (Cu LMM).29,30 The amount of Cu2O relative to Cu0 was greater after desmutting with added CeCl3 and CeCl3 + H2O2 than with nitric acid alone (Table III).

Table III. The relative intensity of copper on the surface of the AA2024 T3 after pre-treatment determined by XPS analysis (% at.).

| Sample | Cu   | Cu2O  |
|--------|------|-------|
| 30 s HNO3 | 99.96 | 0.04  |
| 60 s HNO3 | 95.0  | 5.0   |
| 30 s HNO3 + CeCl3 | 92.7  | 7.3   |
| 60 s HNO3 + CeCl3 | 95.3  | 4.7   |
| 3 min HNO3 + CeCl3 + H2O2 | 97.4  | 2.6   |
| 6 min HNO3 + CeCl3 + H2O2 | 97.6  | 2.4   |
| 9 min HNO3 + CeCl3 + H2O2 | 93.7  | 6.3   |
**Figure 9.** Potentiodynamic polarization curves of the 2024 T3 aluminum alloy after etching followed by desmutting in 1.37 M HNO₃ or 1.37 M HNO₃ + 0.013 M CeCl₃ (a) and 1.37 M HNO₃ + 0.013 M CeCl₃ + 0.029 M H₂O₂ (b), treated for different times.

Figure 10. Potential-current density responses recorded during potentiodynamic anodizing of the AA2024 T3 in 0.46 M H₂SO₄ electrolyte at ambient temperature after desmutting in (a) 1.37 M HNO₃ / 1.37 M HNO₃ + 0.013 M CeCl₃ and (b) 1.37 M HNO₃ + 0.013 M CeCl₃ + 0.029 M H₂O₂.

**Summary**

This study is focused on removal of intermetallic particles from the surface of 2024 T3 aluminum alloy using CeCl₃ additions to a nitric acid desmutting solution. No S-, θ- or Al-Cu-Fe-Mn-(Si) particles were observed on the surface after desmutting for 30 or 60 s in nitric acid with added CeCl₃. In contrast, only S-phase particles were significantly affected by the CeCl₃-free solution. Addition of both CeCl₃ and H₂O₂ to the nitric acid achieved a similar result to addition of CeCl₃, but resulted in slower removal of the particles. Potentiodynamic anodizing in 0.46 M H₂SO₄ solution confirmed the improved surface condition produced by the CeCl₃-containing solutions, with the absence of peaks associated with oxidation of intermetallic particles.

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cathodic current. As the cathodic polarization increases, the diffusion limited current density is reached, which is similar for all specimens, with hydrogen evolution also occurring below −1.1 V (SCE). Since the removal of intermetallics is slower in the presence of hydrogen peroxide, the reduction of the cathodic current for small polarization is greater with increasing desmutting time.

**Potentiodynamic anodizing.—** The potential-current density responses during potentiodynamic anodizing of the alloy in 0.46 M H₂SO₄ electrolyte at ambient temperature with a potential scan from 0 V vs. OCP to 14 V vs. SCE are presented in Figs. 10a, 10b. Two peaks occur after desmutting for 30 and 60 s in nitric acid only: the first, lying close to the OCP, is associated with oxidation of S-phase particles; the second, with a maximum at 4.8 V vs. SCE, is associated with the oxidation of θ-phase (Al-Cu) and Al-Cu-Fe-Mn-(Si) particles (Fig. 10a). With addition of CeCl₃ and CeCl₃ /H₂O₂ to the desmutting solution, these two peaks were absent (Figs. 10a and 10b respectively). Intermetallic particles in the alloy oxidize at higher or lower potentials than the aluminum matrix during potentiodynamic anodizing in sulfuric acid electrolyte. The absence of the peak at 0 and 4.8 V confirms the removal of intermetallic particles in the cerium-containing solutions.

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