



Effects of fluoride ions in the growth of barrier-type films on aluminium



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ABSTRACT

Fluoride ions are commonly present in solutions used in pre-treatments and conversion treatments of aluminium alloys. Because of the intrinsically reactive nature of aluminium metal, alumina layers are either already present on an aluminium surface or form within a matter of seconds on pre-etched aluminium. Hence fluoride ion transport through an alumina layer is an integral part of conversion coating formation. In order to understand the behaviour of fluoride ions in alumina films, the present study investigated the behaviour of fluoride ions during the growth of barrier-type anodic films formed on aluminium at 5 mA cm^{-2} in 0.1 M ammonium pentaborate solution. The films were examined by analytical transmission electron microscopy, scanning electron microscopy and glow discharge optical emission spectroscopy in order to determine their composition and morphology. Fluoride ions were incorporated into the films by adding sodium fluoride to the electrolyte. Additions of up to $3.5 \times 10^{-3} \text{ M}$ sodium fluoride had a negligible influence on the film growth, which occurred at a high efficiency. In contrast, additions of $3.5 \times 10^{-2} \text{ M}$ sodium fluoride reduced the efficiency to about 60%. Dissolution studies demonstrated that fluoride ions had promoted the field-assisted ejection of Al^{3+} ions from the film surface. Using sequential anodizing, the fluoride ions were shown to migrate inwards in the film at a rate about twice that of O^{2-} ions. Thus, a thin fluoride-rich layer of the film was formed next to the aluminium/film interface. Increasing the sodium fluoride content to $3.5 \times 10^{-1} \text{ M}$ led to a porous film formed at a low voltage.

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1. Introduction

Fluoride ions and fluorine-containing anions are commonly present in solutions used for pre-treatments of aluminium alloys, for example in acid cleaning, acid etching and chemical brightening baths [1,2] and also in conversion coating baths, such as chromate [3–5], trivalent chromium [6–8] and fluorozirconate-fluorotitanate [9,10] 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 [11]. 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 [12], titanium [13] and zirconium [14].

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 [15,16]. 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 inwards, with respective transport numbers of about 0.4 and 0.6 [15], it was possible to show that the chloride, bromide and iodide ions migrate inwards more slowly than the O^{2-}

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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 [15]. 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 [16]. 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 [17]. 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 [15]. 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 inwards faster than O^{2-} ions during the formation of amorphous anodic films on tantalum [18] and titanium [19], 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 [18,19]. The relatively fast inwards 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) [20], 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 co-operative 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 described by the high-field conduction equation:

$$J = A \exp(-(Q - zaE)/kT)$$

in which J is the ionic current density, A is a constant at a given temperature, Q is the activation energy, z is the charge on the mobile defect, $2a$ is the jump distance, E is the electric field, k is Boltzmann's constant and T is the temperature [21]. Various atomic models have been proposed to explain the counter migration of the cations and anions [22–26]. However, none of these have 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.

2. Experimental

Specimens of size 3 cm × 2 cm were cut from 99.99% aluminium foil of 0.3 mm thickness. The specimens 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 electropolishing, they were rinsed sequentially in ethanol and distilled water. Following masking with lacquer (Stopper 45 McDermid) to define a working area on one side of 2 cm², 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 [21]. The

electrolyte also results in incorporation of boron species into the film [27], 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 293 K. 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.

Following anodizing, cross-sections were prepared using ultramicrotomy for subsequent examination by analytical transmission electron microscopy (TEM). A Leica Ultracut UCT ultramicrotome was employed, with the section thickness set to a nominal 20 nm. TEM imaging and elemental mapping were carried out on a Titan G80–200 ChemiSTEM (FEI) instrument operated at 200 kV with four energy dispersive x-ray (EDX) spectroscopy detectors. Compositional analysis of films was carried out using EDX analysis (Oxford Instrument XMAX 80) in a FEI Quanta 250 scanning electron microscope operated at either 3 kV or 5 kV. Films were also examined in cross-section and surface views by scanning electron microscopy (SEM) using a Zeiss Ultra 55 instrument operated at 1.5 kV. Cross-sections were prepared using a glass knife to trim the specimens to a suitable thickness, followed by final cutting with a Micro Star type SU diamond knife. The specimens were transferred immediately to the SEM chamber for observing the anodic films. 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. Neon gas was necessary to excite optical emission from fluorine. The wavelengths of the spectral lines used were 396.152 nm (aluminium), 130.217 nm (oxygen), 685.602 nm (fluorine) and 249.678 nm (boron).

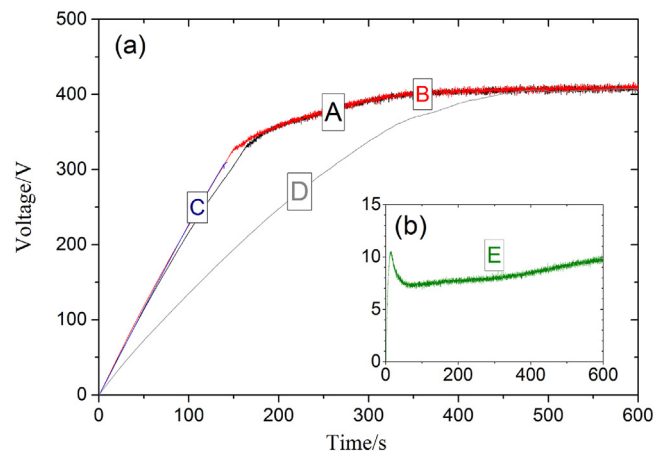


Fig. 1. Voltage-time curves for aluminium specimens anodized at 5 mA cm⁻² in 0.1 M ammonium pentaborate solution at 293 K, with various additions of sodium fluoride. (a) A. No addition. B 3.5×10^{-4} M NaF. C 3.5×10^{-3} M NaF. D 3.5×10^{-2} M NaF. (b) E 3.5×10^{-1} M NaF.

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