

¹⁸O Tracer Study of Porous Film Growth on Aluminum in Phosphoric Acid

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¹⁸O tracer is used to investigate the development of porous anodic films at constant current in phosphoric acid on electropolished aluminum. A barrier layer and porous region form initially with the pore size related to the surface texture of the substrate. Subsequently, major pores emerge, with their sizes related to the anodizing voltage. The evolution of the film is accompanied by increases in growth rate and formation efficiency. The ¹⁸O ions of a preformed oxide are retained in the film during anodization in a nonenriched electrolyte, with ¹⁸O being partitioned among (*i*) the surface region of texture-dependent porosity, (*ii*) the walls of major pores, and, in diminishing amounts, (*iii*) the inner region of the barrier layer. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3490640] All rights reserved.

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The use of ¹⁸O as a tracer species in studies of ionic transport during thermal ¹⁻³ and anodic oxidation^{4,5} is well established. The experiments are carried out by sequentially oxidizing a specimen, for example, first in an ¹⁸O-enriched environment and then in one of the normal isotopic concentration, the natural abundance of ¹⁸O being only ~0.2%. The final location of ¹⁸O can indicate the mechanism of oxygen transport in the growing oxide. The ¹⁸O distribution can be determined nondestructively by nuclear reaction analysis (NRA).⁶⁻⁹ Secondary-ion mass spectrometry and time of flight glow discharge mass spectrometry may also be employed with sputtering of the oxide layers or imaging of oxide cross sections.¹⁰⁻¹⁶

In the present work, ¹⁸O tracer is used with NRA to investigate the formation of porous films on aluminum under mild anodizing conditions. Porous anodic films have been studied extensively due to their importance in the protection of aluminum alloys¹⁷ and, more recently, for various nanotechnological applications. ¹⁸⁻²¹ The films are formed by oxidation of aluminum under anodic polarization, usually in an acid electrolyte. They consist of a thin barrier layer next to the metal and a relatively thick overlying porous layer.^{22,23} In ideal form, the porous layer comprises close-packed, columnar cells of anodic alumina with uniform hexagonal cross sections; each cell contains a central pore running from the barrier layer to the film surface. In reality, the cell arrangement is usually less than the ideal. The barrier layer thickness, pore diameter, and interpore distance are proportional to the anodizing voltage²³ with respective ratios of ~1.0, 1.0, and 2.5 nm V⁻¹.^{23,24} In contrast, under hard anodizing conditions, associated with fast film growth and low electrolyte temperature, the ratios also depend on the current density.²⁵

The most commonly accepted model of porous film growth involves the formation of the alumina due to the ionic migration of Al^{3+} and O^{2-} ions in the barrier layer²⁶ under an electric field of ~10⁸ to 10⁹ V m⁻¹ and the generation of pores by dissolution of the alumina at the pore base.²⁷ The dissolution is accelerated by the electric field and Joule heating compared with the usual chemical dissolution in the electrolyte. However, experiments using a thin layer of tungsten tracer, which is incorporated into the film from the substrate, have suggested that flow of oxide rather than dissolution is important for pore generation.²⁸ Earlier ¹⁸O tracer studies,^{26,29} which employed sulfuric acid electrolyte, showed an anodizing efficiency of ~60% and an inversion of the order of the oxygen iso-

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topes, suggesting a short-circuit mechanism of transport, which is contrary to the mechanism in uniform barrier films.⁴ The use of phosphoric acid in the present experiments enables the formation of cells that are larger than those in films from sulfuric acid, such that the ¹⁸O distribution can be followed in more detail between pore initiation and the establishment of the major pores.

Experimental

Specimen preparation.— Aluminum foil of 99.99% purity [30 Cu, 20 Fe, 20 Si (ppm)] and 0.35 mm thickness (Toyo Aluminum K.K.) with a cubic texture was used in the study. Specimens of dimensions 3×1.5 cm were cut from the foil and then electropolished for 180 s in a mixture of 75% perchloric acid and ethanol (1:4 by volume) at 278 K. Following rinsing with ethanol and deionized water, the specimens were coated with lacquer (Lacomit) to provide a working area of 2 $\,\mathrm{cm}^2$. Subsequent anodizing was carried out at a constant current density of 4.5 mA cm⁻² in 0.4 M phosphoric acid electrolyte (PAE) prepared with 85% H₃PO₄ (Fisher Scientific) and either water enriched in ¹⁸O to 10.0% (CK Gas Products, Ltd.) (electrolyte designated PAE18) or deionized water of the natural isotopic composition (PAE16). pH of both electrolytes was 1.8. A small cell was used to minimize the required volume of O¹⁸-enriched water (30 mL), with the specimen as the anode and an aluminum sheet of area 18 cm² as the cathode. The current was controlled using a dc power supply (Metronix model 6911) connected to a digital multimeter (National Instruments) interfaced to a computer for recording the voltage-time response.

An anodic film was first produced by anodizing at 4.5 mA cm^{-2} up to 20 V in PAE18. The PAE18 was then replaced by PAE16 for a second period of anodizing, either to a selected voltage or for a selected time. In both stages, the current was switched on within 1 min of placing the specimen in the electrolyte. The electrolyte was stirred during anodizing using a magnetic stirrer and was maintained at a temperature of 295 \pm 0.5 K. After anodizing, the specimens were rinsed in deionized water and dried in a cool air stream. A self-supporting anodic film was also prepared by a previously developed method.³⁰ A circular region of 7 mm diameter on one side of an electropolished specimen was coated by lacquer. Following anodizing in PAE18 to 20 V and in PAE16 for 360 s, the lacquer was dissolved in acetone and the exposed aluminum was removed by electropolishing to leave a region of substrate-free film. The specimen was finally rinsed in ethanol and distilled water and dried in a cool air stream.

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Specimen characterization.— Cross sections of the films were prepared by ultramicrotomy for examination by transmission electron microscopy (TEM) using a JEOL FX 2000 II instrument operated at 120 kV. The sections were \sim 15 nm thick. The films were also examined by scanning electron microscopy (SEM) using a Zeiss Gemini Ultra 55 instrument operated at 10 kV with cross sections of the films prepared in an ultramicrotome using glass and diamond knives.

Ion beam analysis of the films employed the Van de Graaff accelerator of the Institut des Nano Sciences de Paris. The analyzed region was usually 1 mm diameter. Rutherford backscattering spectroscopy (RBS) was carried out using 1.8 MeV He⁺ ions, with the ion beam at normal incidence to the specimen surface and a scattering angle of 165°. The data were interpreted using SIMNRA software.³¹ Oxygen contents were determined with the ${}^{18}O(p,\alpha){}^{15}N$ and ${}^{16}O(d,p){}^{17}O$ reactions using 750 and 870 keV ion beams, respectively. The beams were at normal incidence with the detector at 150° to the direction of the incident beam. A 13 μ m thick mylar film placed in front of the detector excluded the detection of elastically scattered ions. Quantification of data employed anodized tantalum references containing $255 \pm 8 \times 10^{15}$ O¹⁸ atoms cm⁻² and $690 \pm 20 \times 10^{15}$ O¹⁶ atoms cm⁻². The precision of the analyses is typically $\sim 3\%$, being determined by uncertainties in the solid angle and the oxygen contents of the references and counting statistics.^{4,6,28,29} Details of the methods have been described elsewhere.⁶ ¹⁸O depth profiling was performed using the exception-ally narrow resonance of the ¹⁸O(p,α)¹⁵N reaction at 151 keV.⁹ An automatic energy scanning system was used to change the beam energy. A 2 mm diameter beam was incident at 50° to the specimen surface with an angle of 90° between the beam and the detector. A 3 μ m thick mylar film excluded elastically scattered protons. ¹⁸O profiles were extracted from excitation curves using the SPACES code.³²

Results

Formation of the anodic films.— Figure 1a shows a typical voltage-time response for a specimen anodized sequentially for the longest time of the present study (~ 375 s). From observations of several specimens, the voltage surges to ~ 2 V at the start of anodizing in PAE18 due to the oxide on the electropolished aluminum and then increases approximately linearly to 20 V at a rate of $1.25\,\pm\,0.05\,$ V $\,$ s^{-1}. Upon changing to PAE16, the voltage rises rapidly to the final voltage in PAE18 and then steadily increases but at a decreasing rate; thus, the average rates are 1.17 ± 0.05 and 1.10 ± 0.05 V s⁻¹ from 0 to 40 V and from 0 to 100 V, respectively. The voltage reaches a maximum between 135 and 145 V and then decreases from ~ 105 to 107 V when anodizing was stopped. The labels S20, S40, S100, Smax, and Sconst on Fig. 1 (used to designate the specimens) indicate the anodizing times for particular specimens; the anodizing data are given in Table I. S20, S40, and S100 were anodized under a rising voltage, Smax to the maximum voltage, and Sconst to the final voltage. Figure 1b compares the voltage responses for specimens anodized with and without interruption, the differences being within the reproducibility of anodizing.

Substrate morphology.— Figure 2 shows the scanning electron micrograph of the aluminum surface with regions of light appearance corresponding to ridges that form due to local differences in the electropolishing rate. The cellular pattern of the ridges arises from the cubic texture of the aluminum with (100) planes parallel to the surface, which will be discussed later. The average cell size was 64 ± 6 nm. The NRA of the surface revealed ~19 × 10¹⁵ oxygen atoms cm⁻², which is equivalent to an ~3 to 5 nm thick film of aluminum oxide/hydroxide.

Film morphologies.— Bright-field transmission electron micrographs of the films attached to the aluminum substrate are shown in Fig. 3 for S20, S40, S60, S100, and Smax. S20 and S60 were anodized in PAE18 only; other specimens were anodized sequentially.



Figure 1. (a) Voltage–time response for aluminum anodized sequentially at 4.5 mA cm⁻² in 0.4 M phosphoric acid at 295 K. (b) Comparing sequential anodizing in PAE18 and PAE16 and anodizing in PAE16 only.

Figure 3a shows a 23-27 nm thick anodic film on S20 with the typical appearance of amorphous anodic alumina. Gentle undulations of the film with peaks separated from 50 to 110 nm follow the texture of the aluminum substrate. Occasional voids were evident along the metal/film interface with lengths up to ~ 30 nm and depth of ~ 10 nm. The voids were common to all the anodized specimens; their origin is uncertain, but they are not considered to be relevant to present interests. Following anodizing at 40 V (S40), the undulations of the film are more pronounced; the film thickness is increased to 47 ± 2 nm at troughs in the film surface, as shown in Fig. 3b, and further increased by ~ 10 nm near the peaks. With anodizing at 60 V (S60), the film surface became strongly scalloped, with film thicknesses at troughs and peaks of 65 ± 4 and 95 ± 8 nm, respectively, as shown in Fig. 3c. The peaks were separated from 50 to 70 nm, similar to previous specimens. Figure 3d reveals a film formed at 100 V (S100), showing features broadly the same as those of S60. The film is 118 ± 4 and 175 ± 7 nm thick at troughs and peaks, respectively. From Fig. 3a-d, the films are thicker at the peak regions of the film surface than at the trough regions, with the difference increasing from ~ 10 to ~ 57 nm between 40 and 100 V. Further, the peak regions correlate with peaks in the metal/film interface. The barrier regions of the films in Fig. 3a-d increase in thickness with increase in voltage, with formation ratios at troughs of $\sim 1.19, 1.08,$ 1.22, and 1.17 nm V^{-1} for S20, S40, S60, and S100, respectively, giving an average of 1.17 ± 0.03 nm V⁻¹. Following anodizing at

Specimen	Potential (V)	Anodizing time (s)	$\begin{array}{c} \text{O RBS} \\ (10^{15} \\ \text{atom } \text{cm}^{-2}) \end{array}$	^{16}O NRA (10 ¹⁵ atom cm ⁻²)	$\begin{array}{c} {}^{18}\text{O NRA total} \\ (10^{15} \\ \text{atom cm}^{-2}) \end{array}$	^{18}O NR - natural ^{18}O (10 ¹⁵ atom cm ⁻²)	$\begin{array}{c} \text{Al} \\ (10^{15} \\ \text{atom cm}^{-2}) \end{array}$	$O^{16} + O^{18} NRA$ (10 ¹⁵ atom cm ⁻²)	P/Al
S20	21	16	126.9	127.2	11.93	11.69	79.9	139.1	0.052
S40	41	35	270.7	257.9	12.05	11.79	165.4	270.0	0.050
S100	101	91	738.9	708.3	12.90	11.74	448.7	721.2	0.051
Smax	140	149	1360.1	1289.2	14.00	11.67	821.7	1303.2	0.057
Sconst	107	385	3809.0	3406.9	17.91	11.35	2305.0	3424.8	0.058
Sconst-ss	107	385		3403.5	18.66	12.11		3422.2	



Figure 2. Scanning electron micrograph of the surface of the electropolished aluminum.

the maximum voltage of 140 V (Smax), regions of increased film thickness are evident, associated with pores up to ~ 200 nm deep and a 154 ± 4 nm thick barrier layer, as shown in Fig. 3e. Elsewhere, the barrier layer thickness is in the range of 165-195 nm, with the film being thicker at peaks by up to ~ 90 nm. Figure 3f shows the scanning electron micrograph of Sconst formed at 107 V (see Fig. 1), revealing well-developed pores with a barrier layer thickness of 117 \pm 5 nm. The total film thickness is 850 \pm 20 nm, with the outer region disclosing fine pores. Small circular voids separated by ~ 100 nm were present in rows on the walls of the major pores, as shown in the inset of Fig. 3f. The formation ratios for the barrier layers beneath the deep pores of Smax and Sconst are ~ 1.10 nm V⁻¹. The dependence of the total film thickness on the anodizing time is shown in Fig. 4, which includes results from specimens additional to the main ones of the study. The data are



Figure 3. Transmission electron micrographs of aluminum anodized in 0.4 M phosphoric acid at 295 K to (a) 20 (S20), (b) 40 (S40), (c) 60 (S60), (d) 100 (S100), and (e) 140 V (Smax). (f) Scanning electron micrograph of -107 V (Sconst). Inset shows secondary pores at walls of major pores.





Figure 4. Dependence of total thickness of the anodic film on the time of anodizing.

approximated by linear regions that intersect at 75 s with slopes of ~ 1.6 and 2.4 nm s⁻¹, the lower rate corresponding to shorter times.

Figure 5a shows the transmission electron micrograph of a planview of the film stripped from S100. A cellular network indicates regions of increased film thickness with cell dimensions from ~ 40 to 165 nm and an average of \sim 70 nm. The scanning electron micrograph in Fig. 5b shows a similar cellular network for Sconst (cell dimensions from ~ 30 to 140 nm and average of ~ 60 nm). The cell dimensions correspond with the morphology of the films in Fig. 3a-e, with the pores developing between the ridges of the textured aluminum (Fig. 2). Dark regions of Fig. 5b correspond to major pores within cells, the pore mouths sometimes being constrained in shape by cell edges. The interpore distance and the dimensions of major pores are typically within the ranges of 150-500 nm and 30-120 nm, respectively. From the measurements of the pore area, the texture-dependent region has a pore volume of $\sim 60\%$, whereas that of the major pores is $\sim 10\%$. Observation of the film base following dissolution of the substrate revealed an average cell size of \sim 267 nm, as shown in Fig. 5c, which is reasonably consistent with the interpore distances at the film surface.

Compositions of films from RBS.— Figure 6 shows the RBS data for specimens anodized according to Fig. 1, together with an example of a spectrum fitted using the SIMNRA program. The spectra reveal edges due to the scattering of He⁺ ions from aluminum, oxygen, and phosphorus at the film surface and from aluminum the substrate, the locations of the latter edges indicating the changing film thickness. The data were fitted by adjusting the ratios of aluminum, oxygen, and phosphorus in the film and the number of atoms per unit area; the results are presented in Table I. The accuracy of data (\sim 5%) is determined mainly by the uncertainty in background signals, the solid angle, and the counting statistics. For S20 and S40, the P:Al atom ratio in the phosphorus-containing film region was derived assuming that phosphorus is present in the outer ~ 0.6 of the film, as found by Takahashi et al.,³³ because the thickness of the phosphorus-containing region was too low for reliable measurement. The results for all the specimens indicate a P:Al atomic ratio of 0.05:0.06 in the phosphorus-containing region, independent of the anodizing time. The analysis is insensitive to hydrogen, for example due to hydroxyl species, water molecules, mono- or dihydrogen phosphate ions, or phosphoric acid molecules in the film material, hydration products, or adsorbed layers. However, hydrogen is considered to be a minor film component. Lanford et al.³⁴ found < 0.4atom % H in films formed in phosphate electrolyte at 368 K. More



Figure 5. Plan-views of the film formed at (a) 100 (S100: transmission electron micrograph) and (b) 107 V (Sconst: scanning electron micrograph). (c) Base of film on Sconst (scanning electron micrograph).

recent thermogravimetric analysis has also suggested a low hydrogen content.³⁵ Further, the present films were formed for short times, which minimizes hydration.

Amount of ¹⁸O in aluminum specimens sequentially anodized for various times.— In estimation of the ¹⁶O and ¹⁸O contents of film, the exchange of ¹⁸O ions between water molecules and phosphate ions in the electrolyte and also between the film and the electrolyte is presumed to be negligible, following the findings of previous studies.^{26,29} The yields from the ¹⁶O(d,p₁)¹⁷O reaction for the specimens S20, S100, Sconst, and the self-supporting film of Sconst-ss



Figure 6. (a) RBS spectra of S20, S100, Smax, and Sconst. (b) Example of spectrum fitted using the SIMNRA program (S100).

(see Fig. 1) are presented in Fig. 7, which also shows yields from the ${}^{16}O(d,p_0){}^{17}O$ and ${}^{12}C(d,p_0){}^{13}C$ reactions. Carbon contents were estimated using the cross-section ratios for the ${}^{12}C(d,p_0){}^{13}C$ and ${}^{16}O(d,p_1){}^{17}O$ reactions measured by Lennard et al., 36 showing an



Figure 7. Proton spectra from the ${\rm ^{16}O}(d,p_1){\rm ^{17}O}$ and ${\rm ^{12}C}(d,p){\rm ^{13}C}$ reactions for S20, S100, Sconst, and S const-ss; deuteron energy 870 keV, charge 10 $\mu C.$

increase in carbon with an increase in the anodizing time from ${\sim}1.3\times10^{16}$ to ${\sim}2.7\times10^{16}$ carbon atoms cm^{-2} between S20 and Sconst. The carbon is considered to be due mainly to the adsorption of hydrocarbons and to increase with pore surface area. Examples of yields for the ¹⁸O(p, α)¹⁵N reaction are shown in Fig. 8a for S20, S100, and Sconst; for specimens with thicker films (Smax and Sconst), account was taken of the reduction of the cross section as protons lose energy in the film, following Amsel and Samuel.⁶ The energy loss was estimated using the measured film thicknesses and the stopping power of amorphous alumina with a density of 3.1 g cm^{-3, 37} calculated by SRIM.³⁸ The results of the oxygen measurements are presented in Table I. The dependence of the oxygen content on the anodizing time is shown in Fig. 9. The data are approximated by two linear regions with slopes $\sim 7.13 \times 10^{15}$ and 9.13×10^{15} atoms cm⁻² s⁻¹ for times <75 and >75 s, respectively. Figure 9 also shows the aluminum contents of the films determined by RBS, which are similarly approximated by linear regions with slopes of ${\sim}4.40 \times 10^{15}$ and 6.56×10^{15} atoms $cm^{-2} s^{-1}$.

The oxygen contents of the films determined by RBS (see Table I) are within 5% of the values determined by the NRA; the latter values are preferred because NRA is more reliable for measurement of elements of low atomic number in the presence of heavier elements. The amounts of ¹⁸O do not change significantly with increasing time of anodizing in PAE16 and are similar to the level in the film formed in PAE18 only (S20). The ¹⁸O enrichment in S20 is



Figure 8. Alpha particle spectra from the ${}^{18}\text{O}(p,\alpha){}^{15}\text{N}$ reaction for (a) S20, S100, and Sconst; proton energy 750 keV, charge 10 μ C. (b) S20, Sconst and Sconst-ss; proton energy 750 keV, charge 30 μ C.

 $9.7 \pm 0.4\%$, which is slightly below the enrichment of the water, due mainly to the presence of phosphate ions in the films.

To evaluate the efficiency of film growth in the early period of anodizing, the oxygen contents were compared for films formed at 16–91 s in 0.1 M ammonium pentaborate electrolyte (ABE) and PAE16. The anodizing times are equivalent to those employed for anodizing S20 to S100. The former electrolyte results in an efficiency close to 100%.³⁹ The ratios of oxygen contents of films formed for the same times in PAE16 and ABE (Table II) suggest an increase in efficiency for PAE16 from ~0.55 to ~0.63.

Depth profiles of ¹⁸O species in films.— The ¹⁸O distributions through the films were determined using the resonance probe. Initial experiments measured the stopping power of the alumina. Figure 10a shows the excitation curve for S20 (PAE18 only). The yield of alpha particles increases steeply near the resonance energy. A shift of 0.5 ± 0.2 keV in the leading edge is due to adsorbed hydrocarbon and any residual oxide/hydroxide from electropolishing. The yield subsequently achieves an approximate plateau and then declines to negligible values. The ratio of the width at half-maximum of the excitation curve and the path length of the beam in the film indicated a stopping power of ~0.127 keV nm⁻¹, which was used



Figure 9. Dependence of the oxygen and aluminum contents films determined by NRA and RBS upon the time of anodizing.

Table II.	Comparison o	f oxygen	contents	determined	by NRA of
specimens	s anodized in A	BE and	PAE16.		

Time (s)	O NRA ABE $(10^{15} \text{ atom cm}^{-2})$	O NRA PAE16 $(10^{15} \text{ atom cm}^{-2})$	$\eta = PAE16/ABE $ (%)
16	244	133	55
35	497	275	55
91	1155	725	63

for fitting all of the present data. In comparison, a stopping power of 0.149 keV nm⁻¹ was obtained for 150 keV protons from SRIM in a film with a density of 3.1 g cm⁻³ containing units of Al₂O₃ and AlPO₄ with a P:Al atomic ratio of 0.05. Figure 10a also shows the fitting of the data using SPACES based on a film containing a constant concentration of 18 O, as depicted in the schematic distribution below the excitation curve. The fitting was achieved with a 24 nm thick film, which satisfactorily agrees with the thickness from TEM (see arrow in Fig. 10), considering also that the TEM thickness may include 2-3 nm of oxide retained from electropolishing. For S40, the majority of ¹⁸O is located in the inner half of the film with roughly one-third in the outer half, as shown in Fig. 10b, in which the ¹⁸O concentration is scaled with respect to S20. The film thickness from SPACES agrees with the result from TEM. For S100, ¹⁸O is enhanced in a ~ 20 nm thick region at the film surface and an ~ 60 nm thick region near the metal/film interface (Fig. 10c). The outer, middle, and inner regions contain ~ 0.25 , 0.20, and 0.55 of the total ¹⁸O, respectively. The film thickness agrees roughly with the result from TEM but may be underestimated due to the significant thickness (~57 nm, constituting ~33% of the film) of the porous region. The films of Smax and Sconst were too thick for the measurement of complete profiles but revealed a near-surface distribution of ¹⁸O similar to those of thinner films, as shown in Fig. 11.

Figure 12 compares the excitation curves for the self-supporting film (Sconst-ss), with the film analyzed from the metal side, and S20. ¹⁸O is present in Sconst-ss in an ~25 nm thick layer near the film base with an enrichment of ~13%. The thickness may be overestimated because the base is scalloped. About 17% of the total ¹⁸O in the film is located in this region. A similar comparison was made using the nonresonant ¹⁸O(p,α)¹⁵N reaction, with Sconst and Sconst-ss analyzed with the beam incident on the original surface and the original film base respectively, as shown in Fig. 8b. The relative position of the peaks reveals that ¹⁸O is mainly buried within Sconst-ss, with most being located nearer to the film surface than the film base.

Discussion

Substrate influences on initial film growth and pore formation.- Electropolishing of aluminum usually creates a surface texture arising from local height differences⁴⁰ with a pattern related to the grain orientation, e.g., cells, asperities, and furrows for (100), (111), and (110) grains. The origin of the texture is uncertain, with suggestions of effects of a mosaic structure within the aluminum⁴¹ and the metal purity,⁴⁰ among other factors. Asahina et al. have also shown that the texture is influenced by the voltage used for electropolishing.⁴² The (100) orientation of the present aluminum provides a uniform texture in comparison with substrates of variable orientation. The growth of the anodic films in PAE proceeds through a sequence of film morphologies. Anodizing at 20 V produces a barrier film with a negligible porosity. With an increase in voltage up to 100 V, the film thickens noticeably above ridges of the aluminum surface, leading to pore arrangements determined by the texture. As the voltage rises further, regions of emerging major pores



Figure 10. Experimental (points) and simulated (solid line using SPACES) excitation curves determined using the resonance at 151 keV of the ${\rm ^{18}O(p,\alpha)^{15}N}$ reaction for (a) S20, (b) S40, and (c) S100. The arrows in the schematic diagrams of the ${\rm ^{18}O}$ distributions denote the thicknesses of the anodic films determined by TEM.



Figure 11. Comparison of the excitation curves determined using the resonance at 151 keV of the ${}^{18}O(p,\alpha){}^{15}N$ reaction for the near-surface regions of S40, Smax, and Sconst.

become increasingly significant and predominant as the voltage declines toward a final steady value. The metal/film interface is shallowly scalloped in the formation of the initial pores, with the bottoms of scallops coincident with the regions of thinner oxide. Deeper scallops develop with the major pores of the film. The general behavior is similar to that reported by O'Sullivan and Wood²³ for the early stages of film growth in PAE at slightly increased current density and temperature. Further, previous work⁴² has also shown the relation between the surface texture and pore development for films formed in oxalic acid, with cell sizes and scallop depths increasing during the initial stages of the oxide growth and with relatively smooth surfaces promoting the initiation of more numerous pores.

Kinetics of film growth.— Figure 4 reveals a slower rate of film growth in the initial period of anodizing than at later times. The average rates, calculated using the difference between the thicknesses of the anodic film and the oxide on the electropolished aluminum (~ 2 nm), were ~ 1.44 , 1.57, 1.60, and 1.89 nm s⁻¹ for S20, S40, S60, and S100, respectively, suggesting an accelerating rate. A final rate of ~ 2.4 nm s⁻¹ (Fig. 4) correlated with the formation of the major pores. The barrier regions of the films increased in thickness with formation ratios of ~ 1.17 and ~ 1.10 nm V⁻¹



Figure 12. Comparison of the excitation curves determined using the resonance at 151 keV of the ${\rm ^{18}O}(p,\alpha){\rm ^{15}N}$ reaction for S20 and Sconst-ss. The latter specimen was analyzed from the metal side.

during the formation of the texture-dependent and major pores, respectively. Because the oxidation of aluminum is the principal anodic reaction, the kinetics indicates that the ratio of the thickness anodic film relative to the thickness of the oxidized aluminum increases as the film evolves. Aluminum oxidizes at a rate of 1.56 nm s⁻¹ during anodizing at 4.5 mA cm⁻² at 100% current efficiency. Thus, in the initial and final regions of Fig. 4, the film grows at ~0.90 and ~1.54 times the rate of metal oxidation, respectively. However, secondary porosity has been observed in films formed in PAE, ^{43,44} leading to pores along cell walls similar to those of Fig. 3f; such pores may result from oxygen generation associated with copper impurity in the aluminum.⁴⁴ Thus, in reality, a small amount of the current may be used in forming oxygen, leading to an overestimation in the previously calculated rate of metal oxidation.

Film compositions and efficiency of film growth.— Ono et al.⁴³ used controlled crystallization of cell walls of films formed in PAE to disclose an amorphous region next to the electrolyte, a partially crystallized intermediate region with both regions containing phosphorus and a highly crystallized phosphorus-free innermost layer. The amorphous region was suggested to be stabilized by protons. Ono and Masuko showed that the phosphorus-containing region increased in thickness with an increase in the anodizing voltage.⁴ Formation at 100 V resulted in phosphorus in the outer ~ 0.78 of the pore wall, with an average P:Al atomic ratio of ~ 0.043 for the film. The latter result is reasonably consistent with the present P:Al ratio of $\sim 0.05:0.06$ and a ratio of ~ 0.05 found previously in the phosphorus-containing region of barrier films formed in phosphate electrolytes at low pH.³³ Assuming a P:Al ratio of 0.05, the average composition of the present films can be expressed as $Al_2O_3 \cdot 0.106AIPO_4$. The average charge number for oxygen is 1.85 due to the incorporation of phosphate ions. The charge number would be reduced by the presence of any HPO_4^{2-} , $H_2PO_4^{-}$, OH^{-} ions, or water molecules. In reality, the phosphorus species may be integrated into the amorphous alumina structure rather than being present in a separate phase.

Figure 9 shows the dependences of the oxygen and aluminum contents of films on the anodizing time, which were approximated by linear regions for times below and above ~ 75 s. The products of the gradients for the oxygen lines and the charge of oxygen ions using a charge number of 1.85 divided by the anodizing current density indicate respective efficiencies of film growth of ~ 47 and $\sim 60\%$. Similarly, the aluminum lines indicate efficiencies of ~ 47 and $\sim 70\%$. Using the results of the efficiencies derived from the measurements of both the oxygen and aluminum contents, the average efficiencies for the two linear regions are ~ 47 and $\sim 65\%$; although in practice, the anodizing efficiency may increase gradually with time over the two regions.

During the growth of barrier-type films at high efficiency, the Al^{3+} ions migrate outward and O^{2-} ions migrate inward, resulting in the formation of alumina at the film surface and film base, respectively. The details of ionic migration in anodic oxides are still uncertain with diffusion of point defects, $\frac{46}{18}$ place exchange of cations and anions,⁴⁷ liquid droplet formation,⁴⁸ and lattice relaxation around oxygen vacancies,⁴⁹ among others being considered. However, irrespective of the precise mechanism, short-circuit transport of oxygen has been unimportant under conditions of uniform ionic current.⁴ The transport numbers of Al^{3+} and O^{2-} ions in anodic alumina have been determined from marker experiments, the values being affected by the anodizing conditions, the nature of the marker, and the method of measurement.⁵⁰⁻⁵⁴ The transport number of Al^{3+} ions has usually been in the range from 0.35 to 0.5.^{51,55-57} Thus, an efficiency of ~ 50 to 65% would be anticipated under conditions in which all outwardly mobile Al³⁺ ions are ejected to the electrolyte, a condition considered critical for pore initiation.⁵⁵ For anodizing in phosphate electrolyte, Takahashi et al.³³ reported an efficiency of close to \sim 50% using phosphate electrolyte at low pH. Under such conditions, an alumina film with a density of 3.1 g cm^{-3} would be \sim 0.83 times the thickness of the oxidized metal, i.e., the product of the Pilling–Bedworth (PBR) ratio of the alumina (1.65) and the efficiency (0.50). The experimental value in the present work (\sim 0.90) may differ from the prediction due to the accuracy of the measurement and uncertainties in the PBR, transport numbers, and film density used to derive the predicted value.

Distributions of oxygen tracer.— The amounts of ¹⁸O tracer species in films formed by sequential anodizing did not change significantly during the evolution of the film between the barrier and porous stages. A similar finding for films formed in sulfuric acid was attributed to a decomposition process of the alumina at the pore base, which resulted in cation transfer only to the solution.^{26,29} The findings of the present work show that in the early stages of the texture-dependent pore development, a large fraction of ¹⁸O is located in a layer near the metal/film interface. However, toward the end stages, ¹⁸O is distributed between an inner region, an intermediate region, and an outer region in proportions $\sim 0.55:0.20:0.25$. The ¹⁸O distribution near the film surface does not change greatly with an increase in the anodizing time and is clearly associated with the texture-dependent porous region. Following the establishment of the major pores in the 850 nm thick film of Sconst-ss, most ¹⁸O was located in the outer half of the film, but ^{18}O was also in a ${\leq}25\,$ nm thick layer near the film base, possibly in the phosphorus-free region, which has a thickness of ~ 23 nm, assuming that it constitutes 20% of the barrier layer.⁴⁵ In comparison with the S100, the proportion of the total O^{18} in the barrier layer has reduced from $\sim\!55$ to $\sim 17\%$ due to the transfer of ¹⁸O to the cell walls.

Origin of porosity.— The authors' previous work using tungsten tracers has suggested that film growth under the present conditions involves flow of film material during the formation of the major pores.^{28,58} The flow prevents tungsten ions from migrating through the barrier layer to the pore base. From studies using various electrolytes, the flow appears to be promoted by incorporation of anion species into the film.⁵⁹ Mathematical modeling has indicated that the material flows downward from beneath the pores and outward toward the cell walls.⁶⁰

The texture-dependent and major porosities differ significantly, with interpore distances and pore volumes of $\sim\!75\,$ nm and 60% and $\sim\!300\,$ nm and 10%, respectively. In a previous work that invokes field-assisted dissolution, 23 pore initiation has been proposed to involve a first stage of enhanced film growth due to preferential oxidation at certain sites of the aluminum substrate. The current subsequently becomes focused at the thinner film regions, where embryo pores are stabilized by a balance between the formation and the dissolution of oxide. However, the present findings (Fig. 3) show less metal oxidation beneath the thickened film than elsewhere. Presuming that isotopic order is conserved at preferentially oxidized sites, ¹⁸O should become buried beneath the ¹⁶O-rich oxide, which is contrary to the observation. The thickness differential of the oxide is therefore suggested to be due to either the displacement of plasticized film material from the thinner regions⁶¹ or the field-assisted dissolution at the thinner regions, which is facilitated by the scalloped texture of the metal/film interface. Tungsten tracer studies may distinguish which is the main process. Flow may be driven by stresses from electrostriction and film growth. Initially displaced material would contain ¹⁸O from PAE18 and, upon change to PAE16, both ¹⁶O and ¹⁸O ions, with near-surface oxide providing mainly ¹⁶O ions, which are incorporated preferentially at thinner regions. At such regions, ¹⁸O ions migrate inward and a proportion of these are near the metal. Most of the ¹⁸O is eventually transported to the cell walls of the major pores, either by migration along the approximately radial directions of the field lines in the barrier layer or by flow of film material from the barrier layer. However, ¹⁸O is still present at the film base of Sconst-ss, when the film is ~ 34 times thicker than the film formed in PAE18 and the length of major pores is ~ 9 times the thickness of the barrier layer; the film base is possibly a region of reduced flow.

The transport processes in porous alumina are probably complex compared with those of barrier films due to nonuniform currents and stresses. A recent theoretical analysis of ion migration by Hebert and Houser⁶² highlighted the importance of mechanical stress, leading to a dependence of transport numbers on current density. Another work has suggested that stress may arise from density variations in the barrier layer.⁶³ Experimental studies have shown a significantly increased efficiency of film growth in PAE between 5 and 30 mA cm⁻²,⁶⁴ with similar findings by Vrublevsky et al. for sulfuric acid.⁶⁵ Such influences of current density may be relevant to the kinetics and efficiency of film growth revealed in Fig. 4 and 9 as the current density changes with changing dimensions of pores. It may be speculated that the simultaneous ionic migration and flow lead to self-regulating but nonuniform distributions of phosphorus species, which are possibly critical to the transition between the texture-dependent and major porosities that depend on the substrate and anodizing voltage.

Conclusions

The growth of anodic films on electropolished aluminum at 4.5 mA cm⁻² in 0.4 M phosphoric acid electrolyte at 295 K occurs with no significant loss of oxygen to the electrolyte between the initial stage of the formation of a barrier film to the final stage of establishment of the major pores of the porous film.

The rate of film growth increases from ~ 1.4 to ~ 2.4 nm s⁻¹ between the commencement of anodizing and the formation of the major pores, which coincides with an increasing efficiency from ${\sim}47$ to ${\sim}65\%,$ expressing the proportion of aluminum species retained within the film.

The thickening of the initial barrier film is accompanied by the development of an outer region of film with an $\sim 60\%$ porosity, followed by the formation of the major pore region with an $\sim 10\%$ porosity. The morphology of the former pores is determined by the texture of the electropolished aluminum.

The ¹⁸O tracer is redistributed by the development of pores. Following the formation of an $\sim 850\,$ nm porous film, 18 O is at the film surface within the cell walls of the major pores and the inner part of the barrier layer. ¹⁸O at the surface is associated with the texturedependent porous region and is relatively constant as the films thicken. In contrast, ¹⁸O of the barrier layer decreases due to transport to the cell walls.

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