Effect of Sealing on the Morphology of Anodized Aluminum Oxide

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ABSTRACT

Ultra-small angle x-ray scattering (USAXS), small-angle neutron scattering (SANS), x-ray reflectometry (XRR) and neutron reflectometry (NR) were used to probe structure evolution induced by sealing of anodized aluminum. While cold nickel acetate sealing and hot-water sealing decrease pore size, these methods do not alter the cylindrical porous framework of the anodic aluminum oxide layer. Hot nickel acetate both fills the pores and deposits on the air surface (air-oxide interface), leading to low porosity and small mean pore radius (39 Å). Electrochemical impedance spectroscopy and direct current polarization show that samples sealed by hot nickel acetate outperform all other sealing methods.

Keywords: nickel acetate sealing; anodic aluminum oxide; ultra-small angle x-ray scattering; reflectometry; corrosion; small-angle neutron scattering.

Introduction

Anodized aluminum displays an unusual porous structure. It is widely accepted that the anodizing film has a two-layer structure—a nonporous barrier oxide and a porous outer oxide. The thin barrier layer (10-100 nm) is found at the bottom of the pores at the metal interface. [1-5] The porous anodized aluminum oxide (AAO) structure is reported to be an ordered hexagonal array of cells with cylindrical pores of diameter 25 nm to 0.3 μm and depths exceeding 100 μm . [6, 7] For low-voltage anodization our recent study by neutron/x-ray reflectometry and small-angle scattering confirms the cylindrical pore structure. In addition, scattering data show that the AAO pore diameter and inter-pore spacing are fixed in the first 10 s of anodizing, after which the pores linearly penetrate the aluminum at constant diameter and spacing. [8] A moderately high porosity of 40% was determined by ultra-small angle x-ray scattering (USAXS) analysis, x-ray reflectometry (XRR) and neutron reflectometry (NR).

Due to the porous nature of AAO films, sealing is necessary [9, 10] to improve corrosion resistance. Sealing strategies based on various combinations of temperature and sealing bath chemistry all improve corrosion resistance to some extent. [10] Sealing traditionally has been done by immersion in boiling deionized water, a method known as hot water sealing. [11-13] The high temperature required and slow kinetics, however, imply considerable energy consumption. [14] As a result the hot water process has been gradually superseded since 1980s by cold sealing. [12] Dichromate and nickel acetate sealing are considered the most effective sealing methods for corrosion prevention. [10] However Cr(VI) is recognized as toxic. [13, 15-17] A number of sealants have been proposed for sealing applications and new sealing processes are emerging. [18]

Recent studies on new sealants and sealing processes include cold nickel acetate sealing, [13] sodium silicate sealing,[18] nickel fluoride sealing, [10, 18] Cr_2O_3 sealing,[19] sodium acetate sealing, [12, 14] cerium acetate sealing, [17, 20] cerium nitrate and yttrium sulfate sealing, [9] sol-gel sealing, [16] and even an expensive sealing process using polytetrafluoroethylene (PTFE). [19] In spite of these efforts to improve the performance, more convenient and effective processes are still needed. [19]

In developing the new sealing methods, DC polarization (DCP) [10, 19, 21, 22] and electrochemical impedance spectroscopy (EIS) [13, 15-17, 20, 23-25] have been used to compare the corrosion performance between different methods. For hydrothermal sealing it is believed that boehmite (AlOOH) is produced at temperatures above 80 °C, while less soluble than hydrargillite ($\text{Al}(\text{OH})_3$) that is formed at low temperatures. For cold sealing methods, however, the mechanism has not been completely elucidated. [18] The structural alternation induced by sealing and the relationship between pore evolution and corrosion resistance have not been investigated.

In this work, we use x-ray reflectivity (XRR), neutron reflectivity (NR), ultra-small-angle x-ray scattering (USAXS) and small-angle neutron scattering (SANS) to investigate the morphological changes induced by sealing. Cold nickel acetate sealing is of particular interest as it has been reported to be a promising alternative to conventional hot water sealing. [10, 13, 17, 20] Our results, however, show that both Ni and high temperature are required for effective corrosion protection.

Materials and Methods

Materials

For the electrochemical performance testing, AA1100 coupons (99.00% Al, from ACT, Hillsdale, MI, USA) were used. Each coupon was cut into 5.08×5.08 cm panels, polished and rinsed in ethanol. These metal panels provide the optimal dimensions and mechanical strength for our electrochemical measurements. For the USAXS and SANS experiments, we used pure Al foils (0.025 mm x 50 mm x 50 mm, 99.45% Al by Alfa Aesar, MA, USA) to insure x-ray and neutron transmission through the samples.

Both NR and XRR require smooth substrates, accounting for the choice of Al-coated Si wafer substrates. One-side-polished single crystal (111) wafers (5.08 or 7.62 cm diameter, and 5 mm thickness) were purchased from Wafer World, Inc. (West Palm Beach, FL, USA). A standard cleaning process (Piranha etching followed by ethanol rinsing) was applied on these wafers. Wafers were rinsed until ethanol did not bead up on the silica surface. Then the wafers were dried in N₂ and stored in sealed container prior to the electron-beam evaporation of the pure Al coating.

Anodizing of Al coupons and foils for USAXS and SANS

In preparation for porous AAO films on AA1100 coupons and pure Al foils, clean samples were dipped in a 20-wt% sulfuric acid at a constant voltage (15 V) controlled by a DC power supply (Instek Test Instrument, San Diego, CA.). A graphite counter electrode was used (5-mm diameter cylinder). The distance between the graphite cathode and anode was fixed at 10 cm. Samples were anodized for maximum time (typically 120 minutes) until current drops to zero, at which time the AAO pores fully penetrate the Al foil. The temperature of anodizing was not controlled. The final samples were air-dried for 24 hours after cleaning in de-ionized water.

Anodizing on Al-coated Si wafers for XRR and NR

The voltage control method used for the coupons and foils proved to be too aggressive for thin Al layers on Si wafers. Therefore, a current-limited, voltage-controlled protocol was used to obtain suitable AAO films on Al-coated Si wafers. This method modifies the conventional constant-voltage anodizing protocol so that AAO film growth can be controlled. [8] If the measured current density during anodizing is lower than the current limit, the voltage will be maintained at the fixed value. Otherwise, the current density will be controlled at the current density limit. An optimized voltage of 15 V and current limit of 0.015 A cm^{-2} were identified previously [8] and used in this study. Samples were anodized at 15 V and 0.015 A cm^{-2} for 30 seconds to reach the maximum AAO thickness without stripping the Al film. These samples were used for XRR and NR studies. As will be described below, these films showed different sealing characteristics compared to the foils formed under voltage-control.

Sealing of anodic aluminum oxide

The AAO films were sealed by four methods: hot water, hot 5 g/L nickel acetate, cold 5 g/L nickel acetate, and cold saturated nickel acetate (180 g/L). The hot sealing methods were used on Al foils and Al coupons only because thin coatings on wafers delaminate at high temperatures. Cold sealing methods were applied on all samples. For hot water and hot nickel acetate sealing, the Al foil/coupon samples were immersed in boiling water (100 °C) or hot nickel acetate (90 °C) for 30 minutes. For cold sealing, the samples were immersed in nickel acetate solutions for 30 minutes at room temperature.

Ultra-small angle x-ray scattering (USAXS) and small-angle neutron scattering (SANS)

The Al foils were used to prepare the anodized and sealed samples for USAXS and SANS experiments. Foils were anodized 120 min in 20-wt% sulfuric acid electrolyte at a voltage of 15

V without current control. We assume that all the aluminum is converted completely into anodized film. The same sealing and cleaning procedure as described for Al coupons was performed on the anodized Al foils.

USAXS was performed at the 15 ID-B beamline at the Advanced Photon Source (APS), Argonne National Laboratories (Argonne, Illinois, USA). SANS was performed at the Lujan Neutron Scattering Center, Los Alamos National Laboratory (Los Alamos, NM, USA) using the LQD instrument.

In USAXS and SANS, we measure the differential scattering cross section per unit volume on an absolute scale, which is referred to as the intensity, $I(q)$, as a function of q , the magnitude of the momentum transfer. The USAXS and SANS data were first subject to an air background subtraction. The USAXS data then were subject to a unified fit [26] using the APS routines.[27] All USAXS data fitting was done on the slit-smeared data using the appropriate resolution function to smear the calculated model. The pinhole SANS data are not slit-smeared.

X-ray reflectometry (XRR) and neutron reflectometry (NR)

Samples for XRR and NR were prepared by anodizing aluminum films deposited on Si wafers. Reflectometry was used to determine the composition and thickness of deposited thin films. The XRR measurements were carried out on the X'Pert PANalytical x-ray reflectometer at the Advanced Materials Characterization Center of University of Cincinnati. NR was performed at the Surface Profile Analysis Reflectometer (SPEAR), Lujan Neutron Scattering Center (LANSCE) at Los Alamos National Laboratory (LANL); and the Liquids Reflectometer (LR), Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL).

In the NR and XRR experiments, a wafer sample is irradiated by the incident beam (neutron or x-ray) at a very small incident angle, θ . The ratio of the fluxes of the reflected beam to the

incident beam is measured as a function of scattering vector, q . The relationship between θ and q is:

$$q = \frac{4\pi \sin \theta}{\lambda} \quad (1)$$

where λ is the wavelength of the incident beam. For Cu $K\alpha$ x-rays, λ is 1.54 Å. For NR, θ is fixed and a broad spectrum of wavelengths impinges on the sample in order to obtain a range of q values. The λ of each detected neutron is calculated by time-of-flight.

The normalized reflected intensity (R) is plotted against q . The $R - q$ curve results from the superposition of waves scattered by the interface. The amplitude and attenuation of each wave are determined by the thickness, roughness and scattering length density (ρ) of each layer.

Thickness and roughness represent structural information while ρ depends on the chemical composition and mass density, d :

$$\rho = d \frac{N_A}{M} \sum_{molecule} b_i \quad (2)$$

where N_A is Avogadro number, M is the molecular weight, b_i is the atomic scattering length of atom i . For x-rays ρ is proportional to electron density, which to first approximation is proportional to the mass density. The neutron scattering length, on the other hand, depends on isotopic composition. This unique character gives substantial contrast on samples with similar mass densities but different composition, such as Al and porous AAO.

The R - q data, analyzed using Irena Macros [27] and MOTOFIT [28], reveal the scattering length density (SLD) profile (ρ as function of perpendicular distance from the substrate). Like all diffraction analyses, the inversion from reciprocal space to real space is not unique. Since more than one SLD profile may fit the data, physical insight and consistency between NR and XRR are required to assure accurate SLD profiles. Since some parameters in the SLD profile are

known, such as the SLD of silicon, the SLD of metal layer and the thickness and roughness of the metal layer, this information eliminates many unrealistic profiles. Furthermore the profiles that we accept evolve reasonably in different conditions ranging from a simple single-layer sample to complex multi-layer films.

Results and Discussion

Effect of sealing on corrosion performance

We investigated the corrosion performance of anodic films (pre- and post-sealing) on Al coupons using dynamic direct current polarization (DCP) and electrochemical impedance spectroscopy (EIS). Three sealing methods (hot water, cold nickel acetate, and hot nickel acetate sealing) were applied on the anodized AA1100 coupons. The hot and cold nickel acetate solutions were all 5 g/L. Solutions were de-aerated for all electrochemical experiments.

The DCP was performed at a scanning rate of 1 mV/s from below open circuit potential (OCP) to above OCP. The cathodic branch was scanned and then the anodic branch. The DCP curves before and after sealing are compared in Fig. 1. For all sealed samples, the corrosion performance improves as revealed by a combination of higher OCP, lower cathodic current density and lower anodic current density. Sealing by hot nickel acetate shows the highest OCP (-0.48 V), while sealing by cold nickel acetate shows the least improvement over the un-sealed sample.

Electrochemical impedance spectroscopy (EIS) measures the ohmic resistance (R_O) and capacitance (C) of the passive films from the current response to an alternating potential. The product R_OC is the characteristic relaxation time.

As expected from the Hoar and Wood models,[29] our EIS spectra typically contain two time constants,[13] which are due to a thin, compact, inner barrier layer and the outer porous layer.

For a system with a 200-Å barrier layer and a 1-μm porous layer, the capacitance of the barrier layer is about $0.5 \mu\text{F}/\text{cm}^2$, while the capacitance of the porous layer (unsealed) is around $0.001 \mu\text{F}/\text{cm}^2$. [29] The capacitance of the water-saturated porous layer is so small that it can only be detected at frequencies higher than 10^7 Hz. On unsealed films, therefore, the measured spectra for frequencies below 10^5 Hz consist mainly of the contribution from the inner barrier layer. [30] Our EIS results on unsealed anodic films are consistent with the above analysis. As shown in the Bode plots (Fig. 2) obtained during exposure to 1-wt% NaCl, we observed one time constant for the unsealed sample as shown by the single maximum in the phase-angle plot (red line in Fig. 2b). Such behavior is observed because the outer layer is “transparent” to EIS due to water intrusion. The capacitance of the dense barrier layer is responsible for the observed time constant. In addition, the total ohmic resistance calculated from the Bode plots (red line) is $1.6 \times 10^4 \text{ ohm cm}^2$, higher than the resistance expected from single porous layer. Therefore, we conclude that the response peak at 10 Hz must be due to the barrier layer postulated by others in anodic films. The phase angles of the sealed samples (blue, black, and purple lines in Fig. 2b) all show two maxima. The response at high frequencies is attributed to the porous oxide layer. The second maximum at low frequency is due to the denser barrier layer at the metal interface. Bode plots also show improvement of the corrosion resistance for sealed samples. The resistance of the barrier (R_b) and porous (R_{p0}) layers, extracted from the impedance data based on the equivalent circuit shown in Fig. 3, are summarized in Table 1. The overall corrosion resistance is measured approximately by $R_b + R_{p0}$. All sealing methods show increased pore resistance (R_{p0}), implying that sealing increases the corrosion resistance, which is generally attributed to filling the pore structure. The resistance of the barrier layer, R_b after sealing also increases, which implies that this layer is porous as well, consistent with the XRR results described elsewhere. [8]

In addition, the capacitances of both the porous and dense layers change for all sealed samples. Therefore, sealing modifies both the porous and dense AAO layers. Hot nickel acetate shows the highest R_{p0} . The improvement by cold sealing with nickel acetate, however, is limited due to the incomplete penetration of the sealing agent into the barrier-layer pores.

Impact of sealing on pore structure

The impact of sealing on AAO pore structure was measured by USAXS and SANS. The results, shown in Fig. 4, lead to similar conclusions from both USAXS and SANS. The AAO structure after sealing by cold nickel acetate and hot water is significantly different from that after sealing by hot nickel acetate, implying different sealing mechanisms. Three-level unified fits of the USAXS data for all samples in Fig. 4a are shown as solid lines, from which the inter-pore distance can be obtained. The details on three-level unified fitting on AAO data can be found elsewhere. [8]

AAO (no sealing)

The AAO structure is commonly recognized as a hexagonal array of straight non-intersecting channels as shown in Fig. 5. Based on the hexagonal structure the porosity can be calculated from the pore radius (R_p) and the inter-pore distance (ζ) by

$$\varphi_p = \frac{\sqrt{3}\pi R_p^2}{2\zeta^2} \quad (3)$$

The volume fraction of pores for AAO before sealing, $\varphi_p = 0.40 \pm 0.02$, is calculated from the measured density (weight divided by volume) of the fully penetrated foil ($2.4 \pm 0.1 \text{ g/cm}^3$) and the theoretical AAO density (3.97 g/cm^3). From pure geometry, the pore radius, R_p , and wall thickness, l_w , are calculated from the interpore spacing determined from the peak position of the SANS data in Fig. 4b ($\zeta = 2\pi/q_{\text{peak}}$) for the AAO data before sealing.

$$R_p = \left(\frac{2\varphi_p \zeta^2}{\sqrt{3}\pi} \right)^{1/2} = 107 \pm 7 \text{ \AA} \quad (4)$$

$$l_w = \frac{2}{\sqrt{3}} \zeta - 2R_p = 108 \pm 10 \text{ \AA} \quad (5)$$

The interpore distance, ζ , can also be calculated by fitting the slit-smeared USAXS data (Fig. 4a) in the region of the peak using the correlated sphere model in the Irena package, which gives $\zeta = 267 \pm 15 \text{ \AA}$, consistent with the inter-pore distance calculated from $2\pi/q_{\text{peak}} = 279 \pm 6 \text{ \AA}$ from the peak position of the curves in SANS data in Fig. 4(b).

Hot water sealing

After sealing by hot water, the quasi-hexagonal structure of AAO remains (Fig. 5a). However the size of the pores must have changed given that the intensity decreases on sealing as shown in Figure 4a. The intensity at the peak decreases by 25% indicating a decrease in porosity after sealing as described below.

To analyze the decrease in intensity, we approximate the system as a simple 2-phase system:

$$I(q=0) = (\Delta\rho)^2 \varphi_p (1 - \varphi_p) \frac{4\pi}{3} R_G^3 \quad (6)$$

where $\Delta\rho$ is the contrast, φ_p is the volume fraction of pores (porosity), and R_G is the Guinier radius, which in our idealized case of oriented pores is the radius-of-gyration of a circle. The contrast, $\Delta\rho$, for a two-phase system is the SLD difference between the solid and pore phases and has a unit of lengh^{-2} . In our case R_G is nearly unchanged at $84.5 \pm 3 \text{ \AA}$ so the ratio of peak intensities before and after sealing is approximated as

$$\frac{I(q_{\text{peak}})_{\text{afterSealing}}}{I(q_{\text{peak}})_{\text{beforeSealing}}} = \frac{(\Delta\rho)^2 \varphi_p (1 - \varphi_p)}{(\Delta\rho)^2 0.40 (1 - 0.40)} \quad (7)$$

Based on the XRR results (not shown), the contrast, $\Delta\rho$ in Eq. (7), does not change on water sealing, so the intensity decrease is attributed solely to the porosity decrease. Knowing that the AAO porosity before sealing is 0.40 ± 0.02 , the porosity decreases to 0.20 ± 0.05 by solving Eq. (7) using Excel Solver. The pore radius and wall thickness are calculated by Eqs (4) and (5) and summarized in Table 2. The values for interpore distance, ζ , from SANS and R_G from a correlated unified fit to the USAXS data are also tabulated. The results show that hot water sealing shrinks the cylindrical pore radius (from $107 \pm 7 \text{ \AA}$ to $76 \pm 5 \text{ \AA}$) with no change in the inter-pore distance. The wall thickness (Eq. (5)) increases from $108 \pm 10 \text{ \AA}$ to $169 \pm 13 \text{ \AA}$ indicating swelling of the skeleton due to hydration.

It should be noted that Guinier radius, R_G , does not reflect the pore diameter as if often assumed. Rather, R_G is proportional to the harmonic mean of $2R_p$ and l_w

$$\frac{1}{R_G} = f \times \left(\frac{1}{2R_p} + \frac{1}{l_w} \right) \quad (8)$$

where f is geometric factor. Based on all the data in Figure 4(a), $f = 0.98 \pm 0.04$.

Cold nickel acetate sealing

For nickel acetate sealing, there is a new component deposited in the pores (Fig. 5b). Therefore the intensity change in Fig.4a is due to a change of both contrast ($\Delta\rho$) and porosity, φ_p , according to Eq. (6).

Using a ρ of $23.2 \times 10^{-20} \text{ cm}^{-2}$ for the AAO before sealing (from XRR measurements below) and $15.46 \times 10^{-20} \text{ cm}^{-2}$ calculated for solid nickel acetate, the average contrast after sealing is a function of porosity as follows.

$$\langle \Delta\rho \rangle = \frac{(1 - 0.40) \times 23.2 \times 10^{-20} + (0.40 - \varphi_p) \times 15.46 \times 10^{-20}}{(1 - \varphi_p)} \quad (9)$$

Assuming constant R_G and solving Eqs (7) and (9) yields a porosity, ϕ_p , of 0.20 ± 0.03 and 0.28 ± 0.03 for saturated and 5g/L nickel acetate sealing, respectively. The calculation differs from hot water sealing in that the contrast, $\Delta\rho$, does not cancel out in Eq. (7). Therefore it is necessary to solve Eqs (7) and (9) simultaneously. After solving for ϕ_p , the pore size and wall thickness are then calculated by Eqs (4) and (5) as tabulated in Table 2.

Hot nickel acetate sealing

As shown in Fig. 4, hot nickel acetate sealing shows significantly different scattering pattern. There is only a faint signature of the original pore structure after hot nickel acetate sealing. Therefore, hot nickel acetate fills the pores and deposits on the air surface (air-oxide interface). The analysis (Table 2) shows very low porosity ($\phi_p = 0.06$) and small pores ($R_p = 39 \text{ \AA}$). The analysis assumes that the pores remain cylindrical, which may not be the case at high pore filling. Isolated pores with low aspect ratio are more likely.

Cold nickel acetate sealing: x-ray and neutron reflectometry (XRR and NR)

Reflectometry probes the morphology of the film normal to the surface and complements the USAXS and SANS data above, which probe morphology in the plane of the film. Due to the thin layers involved however reflectometry presents challenges for the anodization and sealing, either of which may delaminate or strip the Al layer. Exposure to temperatures above 90 °C for example leads to delamination. In addition without a current limit anodization quickly strips the film. To overcome these problems, we used a voltage-controlled, current-limited method for anodization and studied only low-temperature sealing.

We found from USAXS (Table 2) that saturated cold nickel acetate sealing has the largest effect on the original porous AAO structure while still showing substantial scattering from the pore structure. Therefore the saturated system was chosen for further analysis by XRR and NR. The

anodization procedure had to be altered by imposing a current limit to avoid stripping the thin Al layer.

In preparation for cold nickel acetate sealing, anodizing was first performed on 1000-Å Al-coated Si wafers at 15 V in a 20-wt % sulfuric acid at a constant voltage of 15 V for 20 seconds. Since the Al film is thin, the current limit was set at 0.015 A cm^{-2} . Without the current limit, the films strips. The samples were air-dried for 24 hours after cleaning in de-ionized water. Sealing was performed using saturated nickel acetate solutions. The wafers were immersed in the sealing solution for 30 min at room temperature. The samples were rinsed in de-ionized water and dried in ambient before XRR and NR measurements.

In contrast with the USAXS and SANS results, XRR (Fig. 6) and NR (Fig. 7) show little change on sealing. These results indicate that current-limited anodization used for the reflectometry samples leads to a fundamentally different morphology than voltage-controlled anodization without a current limit. This observation is consistent with recent SEM observations on samples anodized by the low-voltage, current-limited method, which show the pores are capped.[8]

Fig. 6 compares XRR on the same sample, before anodization, after anodization and after sealing with cold nickel acetate. Before sealing, four layers on top of Si are required to fit the data: native SiO_2 passive layer, Al with a density of 2.7 g cm^{-3} , barrier-layer AAO (density of $3.5 \pm 0.5 \text{ g cm}^{-3}$), and porous AAO layers (density of $2.8 \pm 0.2 \text{ g cm}^{-3}$). Although the four-layer fit is not perfect, it is possible to reliably extract the thickness and SLD of the porous layer before and after anodization. The 1000-Å Al coating was almost completely converted into AAO on anodization leaving only 20 Å of Al. The density of the porous layer is higher than that observed for the SAXS data ($2.4 \pm 0.1 \text{ g cm}^{-3}$, Fig. 4a), implying a pore volume fraction of 0.30, 25% less than that obtained by SAXS on Al foils.

After sealing, SLD profiles show the four layers on top of Si are also SiO₂, Al, dense AAO (density of $3.0 \pm 0.5 \text{ g cm}^{-3}$), and porous AAO with a SLD of $(23.5 \pm 0.3) \times 10^{-6} \text{ \AA}^{-2}$, which is unchanged from the un-anodized result. Comparison of samples before and after sealing in Fig. 6b also shows that the thickness of the AAO layer remains constant. That is, there is no deposition of the sealing agent on top of the AAO.

Neutron reflectometry is more sensitive to composition than XRR, giving a more sensitive test of pore modification by sealing. NR, however, confirms the XRR result in that the pores are unmodified by sealing (Fig. 7). The porous layer SLD is $3.6 \pm 0.2 \text{ g/cm}^3$, which gives a pore volume fraction of 0.63, assuming un-hydrated Al₂O₃. In addition, NR does not seem to pick up the barrier layer, which is seen in the XRR data (Fig. 6). Hydration of the oxide can reduce the neutron SLD because of the negative scattering length of hydrogen, which may account for the absence of an observable barrier layer.

We attribute the absence of a sealing effect in the wafer samples to closed porosity. SEM of the wafer surface shows only faint dimples without distinct pores. [8] Apparently low-voltage current-limited anodization leads to capping the pores. It is also possible that, because of the very thin Al layer, the pores are not fully formed leading to restrictions that block penetration by the sealing agent.

Conclusions

USAXS results show that cold sealing and hot water sealing reduce the pore diameter, but do not alter the hexagonal pore array. Hot nickel acetate, on the other hand, fills the pores, deposits on the air surface and leaves little remnant of the original hexagonal pore array. For all sealing methods, the pore radius decreases on sealing, but the in-plane distance between pores is unchanged. Hot nickel acetate shows the best corrosion performance as determined by DCP and

EIS, consistent with the filling of the pores. Electrochemical data confirm that both nickel acetate and high temperatures are required for superior corrosion protection.

In contrast with the small-angle scattering results, XRR and NR on saturated cold nickel acetate sealing show no measureable change in the pore morphology with sealing. The absence of a sealing effect is attributed to capping of the pores during anodizing under the low-voltage, current-controlled conditions used to produce the anodized films on Si wafers. These results show that there is interplay between anodization protocol and sealing protocol that precludes generalization. The scattering methods demonstrated here are powerful tools suitable for sorting out such issues.

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FIGURES

Figure 1. DCP for anodic films with and without sealing (in 1 wt % NaCl, de-aerated aqueous solution). All samples were conditioned at OCP for 30 min and then scanned in the noble direction from the lowest potential. The scan rate was 1 mV/s. Hot sealing in nickel acetate (purple) yields the highest OCP and the lowest anodic current density. The hot and cold nickel acetate solutions were all 5 g/L.

Figure 2. Bode plots for virgin and sealed anodic films. The solid lines are the impedances and the phase angles; the dashed lines are fits from the equivalent circuit. The unsealed sample shows only one time constant. The sealed samples (black, blue, and purple lines in (b)) show two maxima, consistent with increased pore resistance R_{p0} . The hot sealing methods improve the corrosion resistance more than the cold method as shown by the increase of $R_b + R_{p0}$ of the sealed samples. The hot and cold nickel acetate solutions were all 5 g/L. R_b is the barrier layer resistance.

Figure 3. Equivalent circuit of anodized Al alloys. R_{p0} is the ohmic resistance of porous layer, R_b is the ohmic resistance of barrier layer, C_{p0} is the capacitance of porous layer, and C_b is the capacitance of barrier layer.

Figure 4. (a) Slit-smear USAXS and (b) pin-hole SANS data on through-thickness AAO samples sealed by different methods. The intensity is the absolute differential scattering cross section (cm^2) per unit sample volume (cm^3) and thus has units of cm^{-1} . The solid lines are 3-level unified fits of the USAXS intensities. All samples were exposed for 30 min. Except for sealing by hot nickel acetate, all data show correlation peaks at $q = \sim 0.02$ and ~ 0.04 $\text{\AA}^{-1}$, due to the formation of the porous structure. Fitting of the correlated peaks in Irena package gives the value of correlation range, ζ . [8]

Figure 5. Schematic top views of the structural features of (a) AAO before sealing and AAO after sealing by hot water, and (b) after sealing by nickel acetate solutions. Pore diameter ($2R_p$), wall thickness (l_w) and inter-pore distance (ζ) are determined from the parameters obtained from the unified fit of the USAXS data. $\zeta = a\sqrt{3}/2$ is the spacing between the (11) planes of the 2-dimensional hexagonal lattice with constant $a = 2R_p + l_w$. In a previous study[8] we took ζ to be the distance between the (10) planes.

Figure 6. (a) XRR data and (b) SLD profiles of the Al-coated Si wafers. The data are shifted on the ordinate for clarity. The anodized sample before sealing (blue, anodized in sulfuric acid at 15 V for 20 seconds), and after sealing (red, sealed in saturated nickel acetate for 30 minutes) are compared with the bare Al sample (black, 1000- $\text{\AA}$ pure Al coated wafer). The data show minimal change after 30-min sealing.

Figure 7. (a) NR data and (b) SLD profiles of the pure Al-coated Si wafers. The same anodized sample before and after sealing in cold saturated nickel acetate for 30 min are compared with the bare Al sample. The data show no change of the porous layer on sealing, which is attributed to capping of the pores when anodized under low-voltage, current-controlled conditions.

TABLES

Table 1. Estimated resistance of porous layer (R_{p0}), resistance of barrier layer (R_b), capacitance of porous layer (C_{p0}) and capacitance of barrier layer (C_b) from the EIS spectra.

Anodic film	R_{p0} (ohm cm^2)	R_b (ohm cm^2)	C_{p0} ($\mu\text{F} / \text{cm}^2$)	C_b ($\mu\text{F} / \text{cm}^2$)
Unsealed	1.38×10^4	2.89×10^3	5.27	16.44
Sealed by cold nickel acetate	2.04×10^5	1.53×10^4	21.02	1.05
Sealed by boiling water	1.04×10^6	9.03×10^4	10800	0.02
Sealed by hot nickel acetate	7.40×10^6	4.54×10^4	24.10	0.02

Table 2 Pore size, wall thickness, and inter-pore distance of the through-thickness AAO foils after sealing by different methods (30 minute immersion for all samples). NiAc stands for nickel acetate. The parameters for interpore distance, ζ , and Guinier radius are extracted from the SANS and USAXS data. The porosity for AAO (no sealing) was calculated from the density of the fully penetrated film. The porosities for other sealing methods were calculated using Eq (7) from the USAXS intensities in Fig.4a. Numbers are not reliable for hot nickel acetate sealing due to the weak scattering from the pore structure. The errors for R_G , and l_w are calculated from error propagation in Eqs (4) and (5). Also $2R_p + l_w = 2\zeta / \sqrt{3}$. The physical meaning of R_p , l_w , and inter-pore distance, ζ can be found in Fig. 5.

Sample	Porosity, ϕ_p	Pore size, R_p (Å)	Wall thickness, l_w (Å)	Inter-pore distance, ζ (Å)	Guinier Radius, R_G (Å)
AAO (no sealing)	0.40 ± 0.04	107 ± 7	108 ± 10	279 ± 5	82 ± 4
cold NiAc (5g/L)	0.28 ± 0.03	89 ± 8	144 ± 17	279 ± 5	81 ± 4
cold NiAc (saturated)	0.20 ± 0.03	78 ± 8	181 ± 17	292 ± 5	81 ± 4
hot water	0.20 ± 0.04	76 ± 5	169 ± 13	279 ± 5	87 ± 4
hot NiAc	0.06 ± 0.03	39 ± 10	236 ± 50	272 ± 10	85 ± 10