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Non-destructive characterization of corroded glass surfaces by spectroscopic ellipsometry

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ABSTRACT

Characterization of the alteration layers that form on glass surfaces during corrosion processes provides valuable information on both the mechanisms and rate of glass alteration. In recent years, state-of-the-art materials and surface characterization techniques have been employed to study various aspects of the alteration layers that result from corrosion. In most cases, these techniques are destructive and thus can only be employed at the end of the corrosion experiment. Here, we show that the alteration layers can be investigated by non-destructive spectroscopic ellipsometry (SE), which provides pertinent information on alteration layer thickness, morphology, and, through correlation of the index of refraction, porosity. SE measurements of silicate glass coupons altered in aqueous solutions of pH 3, 5, 7, 9, and 11 at 90 °C for 7 days are compared to cross-sectional secondary electron microscopy images. In most cases, quantitative agreement of the alteration layer thickness is obtained. The fractional porosity calculated from the index of refraction is lower than the porosity calculated from elemental analysis of the aqueous solutions, indicating that the alteration layer has compacted during corrosion or the subsequent supercritical CO₂ drying process. These results confirm the utility of performing non-destructive SE measurements on corroded glass surfaces.

1. Introduction

Man-made silicate glasses exhibit extremely high durability, surviving for thousands of years in the natural environment [1,2]. Nonetheless, these glasses exist as a thermodynamically metastable phase, and when in contact with aqueous environments such as groundwater, they irreversibly transform into more stable phases [3]. This corrosion has a substantial impact on the design of disposal systems for nuclear wastes immobilized in glass [1,3,4]. It is impossible to measure the corrosion behavior of a given glass composition in the laboratory over the timescales expected for disposal (up to tens or hundreds of thousands of years). Instead, shorter-term corrosion, dissolution, and leaching experiments are undertaken to develop robust dissolution rate models which can then be extrapolated to long time scales [5].

Corrosion of silicate glasses in contact with aqueous solutions [1,5–7] consists of ion exchange between hydrogen-containing solution ions (e.g., H⁺, H₃O⁺) and mobile glass ions (e.g., Na⁺, Li⁺, K⁺) and the hydration and corrosion of glass forming components, and is strongly influenced by transport of solution and glass components to and from the reacting glass surface, as well as formation of solid alteration

products. These processes can result in chemical and physical property gradients at the altered glass surface. Traditional corrosion studies have utilized high surface area glass powder in contact with the aqueous solution at elevated temperature (see for example ASTM C1285 [8]); the rate and mechanism of corrosion are inferred from elemental analysis of the glass components in solution. While this remains an important facet of glass corrosion work, powders are not amenable to detailed characterization of the compositional and morphological properties of the altered glass surface. Modern work on corrosion of glass monoliths has allowed surface science characterization methods to be used to directly investigate the thickness and composition of the alteration layer(s) in detail. As one example, Gin et al. [9,10] studied a monolithic borosilicate glass (SON68) that had been altered in controlled laboratory conditions for 25.75 years. Investigation of the alteration and surface layers at the end of the experiment with cross-sectional transmission electron microscopy (TEM), energy-filtered TEM, Raman microspectroscopy, nanoscale secondary ion mass spectrometry (nanoSIMS), and atom probe tomography (APT) revealed that glass corrosion did not occur in a uniform, homogeneous manner [11] as predicted by simple corrosion models. Instead, these techniques

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revealed that the “alteration layer” exhibited a complex, multilayered structure. Other recent works [12–15] utilizing state-of-the-art surface analysis techniques have continued to explore the details of alteration layer formation during glass corrosion. The results of these studies have even led to the proposal of entirely new glass corrosion models [16–18].

Spectroscopic ellipsometry (SE) is a non-destructive technique to measure the layer-resolved thickness and optical properties (index of refraction, n , and extinction coefficient, k , or analogously the real and imaginary parts of the dielectric function, $\tilde{\epsilon}$) of thin film structures [19,20]. Because the optical properties of a solid are governed by its composition and density, measurement of the complex optical properties of a sample can provide direct morphological and electronic structure information, as well as inferred compositional details. The SE measurement consists of elliptically polarized light which is incident on a flat sample surface at an oblique angle ($> 45^\circ$ from the sample normal). Interaction of the light with the sample leads to both polarization rotation (Ψ) and phase difference (Δ) of the specularly reflected light. These differences are determined by the optical properties of the sample, and can be related to the reflectivity of the sample through the complex reflectance ratio, ρ :

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta} \quad (1)$$

where r_p and r_s are the reflectivity of p - and s -polarized light, respectively. SE measurements are collected near the Brewster angle, where r_p goes to zero but r_s remains large. Through the Fresnel equations, ρ can be related to the complex refractive index of the sample of interest. Optical models consisting of one or more distinct layers on the sample surface can be developed to simulate the experimental $\tan(\Psi)$ and Δ data (through application of the Fresnel equations for each layer), and fitting algorithms are often used to determine the layer thicknesses and/or optical properties which best simulate the experimental data. In simpler cases, the optical properties are known, and the layer thickness can be fit. In more complicated cases, both the thickness and the optical properties must be determined by modeling.

SE has been widely applied to thin film deposition and metrology [21–24], including the analysis of coatings on glass [25,26]. However, SE has rarely been applied to the study of the alteration layers that develop on glass surfaces exposed to aqueous environments. Feldmann et al. [27] used ellipsometry to characterize the corrosion of float glass by water during processing and storage. The optical properties of the alteration layer could be modeled only by including a gradient in the index of refraction from the pristine glass interface ($n = 1.52$) to the surface of the alteration layer ($n = 1.46$); this gradient in optical properties was attributed to the concentration gradient in the alteration layer. Portal et al. [28] studied the corrosion of an alkali silicate glass relevant for nuclear waste immobilization. After leaching experiments in 1 M HCl for 0.5–72 h, good agreement was obtained between SE and SIMS characterization of the altered layer thickness, and both techniques were sensitive to a thin surface layer which presumably arose as a result of polishing. The alteration layer thickness calculated from measurement of extracted Na in solution was consistently larger than those determined by both SE and SIMS; after leaching for 24 h at 60 °C, the alteration layer equivalent thickness calculated from the Na in solution ($\sim 10 \mu\text{m}$) was 42% larger than the layer measured by SE ($\sim 7 \mu\text{m}$).

In this paper, we present a comparison of the alteration layer thickness measured by SE and cross-sectional secondary electron microscopy (SEM) of the International Simple Glass (ISG) [3], after corrosion in aqueous solutions at various pH values. Modeling of the SE data is able to quantitatively reproduce the alteration layer thickness in a non-destructive measurement, and provide an estimate of the fractional porosity of the layer. Comparison of these values to those estimated from elemental analysis of the aqueous solution reveals that the alteration layer has compacted. The possibility of performing non-destructive, time-resolved alteration layer measurements of the same glass

sample periodically during long-term corrosion experiments (*ex situ* or *in situ*) is also discussed.

2. Experimental

Static corrosion experiments were conducted on ISG, a simplified glass composition chosen with input from the international scientific community involved in glass corrosion studies [3]. ISG contains the primary components in borosilicate glasses currently under consideration or being utilized for nuclear waste immobilization *via* vitrification. The composition of ISG is approximately 18.0 atomic % Si, 9.7% B, 7.7% Na, 2.2% Al, 1.6% Ca, 0.5% Zr, and the remainder O [3]. Coupons of ISG approximately 1 cm \times 1 cm by 0.1 cm were cut, and the large faces were polished to $\frac{1}{4}$ micron with diamond paste (Ted Pella). Solutions were initially made to pH values 3, 5, 7, 9, and 11 (within 0.2) at room temperature with target ionic strength values of 2 mM. Solutions at lower pH's (3, 5) were buffered with potassium phthalate, and solutions at mid pH's (7, 9) were buffered with tris(hydroxymethyl)aminomethane. The pH of the solutions was adjusted with HNO₃ and KOH. The pH 11 solution had no buffer, but KNO₃ salt was added to maintain ionic strength of 2 mM. The solutions were heated to 90 °C, and then solution pH values were checked and adjusted to target pH values (within 0.1) using KOH or HNO₃. The final ionic strength varied from 3.9 mM to 8.6 mM. Coupons were inserted into Savillex® vials containing 10 mL of the pH-adjusted solutions to obtain a glass-surface-area-to-solution-volume ratio (S/V) of 25 m⁻¹. The coupons were suspended by a Pt wire in the solution so that all faces were equally exposed. The wire was attached to the coupon using a small amount of glue (Loctite® Plastics Bonding System); this covered area was not subtracted from the surface area calculations. Experiments were conducted in an oven heated to 90 °C for 7 days without disturbing the samples. At the conclusion of the alteration experiments, the solutions were removed and the glass coupons were dried using supercritical CO₂ to preserve the structure of any porous gel layer which may have formed. The final pH values of the solutions were measured at 90 °C. Table 1 shows pH values of the solutions at the start and end of each experiment. Because the aqueous solutions were only weakly buffered, ISG corrosion over the course of the 7-day alteration period caused all solutions to become more basic.

Aliquots of final solutions were diluted with 0.1 to 0.3 mol-L⁻¹ HNO₃ and analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent® 5100 RV) for Al, B, Ca, K, Na, and Si; the instrument was calibrated using dilutions of standard solutions (Inorganic Ventures). Equivalent thicknesses (Eth , in μm) for altered portions of altered glasses were calculated using Eq. (2) with boron as a tracer:

$$Eth_B = \frac{C_B}{\frac{S}{V} f_B \rho_0} \quad (2)$$

where C_B is the boron concentration in g·m⁻³, f_B is the mass fraction of boron in ISG, S/V is glass-surface-area-to-solution-volume ratio in m⁻¹, and ρ_0 is the initial density of ISG in g·cm⁻³.

Spectroscopic ellipsometry data were collected with a variable angle spectroscopic ellipsometer (V-VASE, J.A. Woollam, Inc.) at incident angles of 65°, 70°, and 75° from the sample normal and photon energies

Table 1
Solution pH values at the start and end of alteration experiments, measured at 90 °C.

Nominal corrosion conditions	Initial pH	Final pH
pH 3	3.00	5.27
pH 5	5.09	6.49
pH 7	7.16	7.45
pH 9	8.99	9.23
pH 11	11.10	11.34

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