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Effect of glass composition on the hardness of surface layers on aluminosilicate glasses formed through reaction with strong acid

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Abstract

The effect of glass composition on physico-chemical properties of surface layers formed through reaction between strong acid and several silicate and aluminosilicate glasses was studied through transmission-IR, ATR-IR, XPS, SIMS, and nano-indentation analyses. It was shown that aluminum is depleted from the surface while molecular water is diffused into the surface layer of glasses with high levels of aluminum. Nano-indentation experiments indicated that the hardness of the surface layers were decreased compared to that of the bulk region and the degree of the softening was more significant in the high aluminum glass.

KEYWORDS

aluminosilicates, corrosion/corrosion resistance, glass, spectroscopy, surface

1 | INTRODUCTION

The aluminosilicate glass system is important for industrial glass products, nuclear waste glass and for understanding natural glasses in the Earth's crust. For some applications, high durability in strong chemical solution is required. Although the incorporation of aluminum oxide improves the durability of glasses to some extent, too much aluminum is known to degrade the acid durability of glasses.[1-3] This can be attributed to the high solubility of Al^{3+} in strong acid and the low activation energy for bond rupture in the AlO_4 structural unit.[4] However, the properties of the leached surface layer formed through strong acid treatment is not well investigated. In Hamilton's study,[3] it was found that in strong acid, the most important parameter controlling the leaching and dissolution behavior of aluminosilicate glasses was the number of Al–O–Si linkages present in the bulk glass structure. In the glasses containing high amounts of aluminum (which also have a large number of Al–O–Si linkages), dissolution is dominant over leaching in acid conditions. Mellott reported that, although a silica-rich layer was formed on aluminosilicate glass surfaces after strong acid treatment, no evidence supporting the diffusion-controlled reaction was reported[5]; i.e., both Al and network modifier ions were all depleted to the same depth, and with continued exposure to acid, they became completely devoid of all components except silica and hydrous species. Although the altered surface layer on aluminosilicate glasses formed after acid treatment was reported to contain 6-coordinated Al species from nuclear magnetic resonance (NMR) studies,[2,3] the existing state of hydrogen and the speciation of hydrous constituents in the surface layer have not been analyzed so far.

Several methods have been reported for the analysis of water, hydroxyl and hydrogen in glass, all of which rely largely on vibrational spectroscopies such as IR and Raman analyses. Although the speciation of water in the bulk glass is commonly evaluated with transmission IR or NMR,[6-11] the methods lack the surface sensitivity needed to reveal the speciation of water in the surface region of a flat glass. Attenuated total reflection infrared (ATR-IR) spectroscopy is a method that can provide a surface-sensitive analysis in the outermost micron of the surface.[12] We reported that Si–O–Si network alterations at surfaces, for example, due to

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