

I. INTRODUCTION

The strength and fracture behavior of silica and silicate glasses can be influenced by surface chemistry in many different ways. It may be appropriate to start this discussion by attempting to identify the most important relationships.

- (1) Surface chemical phenomena can result in compositional and structural changes at glass surfaces *during high temperature fabrication* processes. In the case of silica glass, this is limited to chemical adsorption of water and other gaseous species, as well as surface segregation and/or volatilization of water and impurities from the

bulk of the glass. In the case of multicomponent glasses, more dramatic composition changes may occur due to the mobility and reactivity of the modifier species. The extent of chemical and structural modification at the surface is a complex function of the bulk composition of the glass and the thermal and atmospheric history of the glass surface. Obviously, any high temperature chemical or structural alteration of the surface will influence subsequent adsorption and surface chemical behavior in a manner which cannot be predicted simply from a knowledge of the bulk glass composition. It will be shown, for example, that for a given glass composition, some high temperature fabrication processes enhance the hydration resistance of the surface while others degrade it.

- (2) The chemisorption of gaseous species at surfaces and crack-tips *under residual or applied stresses* can contribute to the rupture of interatomic bonds. This phenomena is, of course, fundamental to slow crack growth and will not be treated in any detail here. However, it is worth pointing out that slow crack growth does exhibit a composition dependence. Thus, the strength behavior of real glass surfaces will be influenced by any in-depth modification of the surface during high temperature fabrication.
- (3) Chemical reactions between the glass surface and adsorbed species can lead to broken bonds, hydration films and other structural heterogeneities at the surface *under ambient conditions*. These reactions will undoubtedly be localized at high energy surface sites, especially those associated with strained bonds. And while all the bonds at the surface may be strained to some extent, the strain may be accentuated at regions associated with bulk topological features, phase separated regions, crystallites or impurities. The distinction between this phenomena and slow crack growth is perhaps philosophical since both involve bond breaking chemical reactions at high energy surface sites. However, it has a special significance in the sense that it may be a realistic source of flaws, or flaw-precursors, and may in some instances occur at high energy sites not associated with strained bonds per se. The alkali species in multicomponent glasses, for example, will preferentially react with water and carbon dioxide. The reaction and distribution of surface reaction products and corrosion pits will be non-uniform to an extent determined by the composition and thermal history of the glass.

In general, one expects these kinds of interactions to be autocatalytic in the sense that any subsequent chemical reactions will

also be localized at these sites. For example, the reaction between a strained siloxane linkage ($\equiv\text{Si-O-Si}\equiv$) and water not only leads to a broken bond, but the silanol groups ($\equiv\text{Si-OH}$) so-produced will enhance the physical adsorption of water at that same site. This relatively mobile water is then available to react with other siloxane linkages in that region whether they are strained or not.

- (4) The mechanically induced 'flaws' at glass surfaces are high energy sites where the adsorption and/or condensation of mobile water can result in corrosion reactions. That is, the chemistry of the condensed water can be modified dramatically by the dissociation of surface silanol groups and ion-exchange reactions with modifier species due to the high ratio of surface area to solution volume. Thus, the *geometry of the flaw* may be modified by gel formation and swelling, non-uniform dissolution, and etching.
- (5) The physical adsorption of mobile water or other gaseous species at pristine surfaces, at compositionally-modified surfaces, on surface reaction products, within pre-existing flaws or at the interface between the glass surface and organic coatings provides a *reservoir of reactants for chemical interactions upon the application of stress*. It is well known from a wide variety of fracture mechanics studies that the transport of water or other reactants can limit slow crack growth. It is possible that the most significant influence of hydrated surface layers — especially within microcracks — is their capacity to 'store' physically adsorbed water until a stress is applied. This 'reservoir of reactants' becomes especially significant when it exists at the interface between a glass fiber and organic coating.

Obviously, one cannot be too dogmatic about these classifications since they are all dependent upon the same fundamental phenomena. However, these classifications do facilitate the design of critical experiments, and perhaps most importantly, the interpretation of strength behavior for commercial glass products.

It becomes immediately evident that melt surfaces and fracture surfaces are most appropriate for experimental investigation. The melt surfaces of glass are among the strongest surfaces available and the most prevalent in practice. Most importantly, though, it is the strength behavior of these surfaces which is most dependent upon chemical interactions. Understanding the way in which these surfaces evolve at high temperature, during cooling, and during exposure to and service in the ambient atmosphere, is extremely important but not well established. Fracture surfaces, on the other hand, are most useful as 'model' surfaces for studying the evolution of melt surfaces and the behavior of cracks and crack-tips in the absence of stress.