Journal of Non-Crystalline Solids 379 (2013) 161–168

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Environmental effects on fatigue of alkaline earth aluminosilicate glass with varying fictive temperature

Simon Striepe [a], Joachim Deubener [a,*], Morten M. Smedskjaer [b], Marcel Potuzak [c]

[a] Institute of Non-Metallic Materials, Clausthal University of Technology, 38678 Clausthal-Zellerfeld, Germany
[b] Section of Chemistry, Aalborg University, DK-9000 Aalborg, Denmark
[c] Science and Technology Division, Corning Incorporated, Corning, NY 14831, USA

ARTICLE INFO

Article history:
Received 20 June 2013
Received in revised form 1 August 2013
Available online 2 September 2013

Keywords:
Aluminosilicate glasses;
Fictive temperature;
Crack initiation;
Slow crack growth;
Environmental fatigue

ABSTRACT

The influence of relative humidity on microhardness, stress intensity, crack resistance, and sub-critical crack growth of an alkaline earth aluminosilicate glass has been studied by Vickers indentation. Quenched and annealed glasses with a wide range of fictive temperatures ($\Delta T_f \approx 130$ K) are compared in order to determine the influence of the thermal history on these properties. Vickers hardness is found to be essentially unaffected by the environmental conditions, while the stress intensity factor (fracture toughness) and the crack resistance decrease significantly with increasing humidity. The glasses with lower fictive temperature exhibit a larger change in the micromechanical properties when comparing wet and dry conditions. Finally, it is found that sub-critical crack growth is larger in the low fictive temperature glasses, indicating a diminished resistance against fatigue and stress corrosion.

1. Introduction

The glass surface is the most important part of the glass material for a large range of technological applications, e.g., when glass is used as cover material for personal electronic devices, as substrate for solar cells or as a backplane for thin-film-transistor liquid-crystal displays (TFT LCD). However, a complete understanding of the structure of glass surfaces is still lacking. This is due to the complexity of atom rearrangements at the surface, diffusion of mobile ions to and from the surface, and the consequent roughening and nanostructure formation [1]. Most importantly, the presence of flaws at the glass surface limits the glass mechanical properties. Intrinsically glass constitutes the strongest man-made material that can be produced on a large scale [2]. However, the glass surface is vulnerable against chemical reactions with the environment (particularly H_2O) and mechanical damages (scratches, indents, cracks, etc.), which limits the practical glass strength to typically ≈ 50 MPa. Hence, it is important to understand and control the parameters that degrade glass strength [3]. In this work, we provide new insights into the influence of atmospheric humidity on the indentation-derived micromechanical properties of a poly-silicone (p-Si) substrate glass with varying thermal history (as quantified by the fictive temperature, T_f).

Orowan [4] suggested that the static fatigue of glasses in humid atmosphere can be related to the water diffusion and adsorption at the crack tip, which results in a decrease of the fracture surface energy. The influence of atmospheric humidity on the cracking behavior of soda–lime–silicate glasses was studied for the first time in 1967 by Wiederhorn [5], who attributed the fatigue phenomenon to sub-critical crack growth (SCCG). SCCG is enhanced by stress corrosion, where the silicon–oxygen-bond is assumed to undergo a hydrolysis reaction. The reaction product is responsible for the mechanical strength degradation, leading to a more pronounced SCCG. In the following decades, significant attention was paid to the cracking behavior of glasses under various environments with different molecular structure (lone pair orbital) [6,7] and pH-value [8].

Hirao and Tomozawa [7] found that water enters into the glass during the mechanical testing (indentation), which causes softening of the glass, while other liquids do not. This entry of water into the glass was confirmed by hydrogen concentration depth profiles on the fracture surface of a silica glass by Tomozawa et al. [9], since a higher hydrogen concentration was found in glass surfaces fractured in water in comparison with oil. The water diffusion into the glass was also found to depend on the fictive temperature [10]. Thus, the greater tendency to mechanical fatigue in low-fictive temperature glasses may be explained by the enhanced water entry, which promotes the fatigue behavior [11].

In the case of silica fibers, calculated fatigue parameters show that a simple exponential function describes best the crack growth for varying humidity and that the strength and fatigue of coated and as-prepared fibers exhibit similar humidity dependences [12]. The impact of water partial pressure on the cracking behavior of silicate glasses was found to depend primarily on the susceptibility of the glass towards water adsorption at the surface and water permeation into the glass volume [13]. An important feature of glasses in this aspect is their interaction

* Corresponding author. Tel.: +49 5323 72 2463; fax: +49 5323 72 3710.
E-mail address: joachim.deubener@tu-clausthal.de (J. Deubener).

0022-3093/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnoncrysol.2013.08.005

with water from the atmosphere. Consequently, in hygroscopic glasses, such as phosphates, a high water uptake rate leads to promotion of crack growth [14], while a reduction in the ion mobility of mixed alkali/alkaline earth oxide glasses decreases the water absorption and subsequently decelerates SCCG [15].

Vickers indentation is a commonly applied method for determining micromechanical properties of glasses (see e.g. reviews in refs. [16] and [17]). During indentation, three deformation processes take place: (1) elastic deformation of the surface, which is completely recovered upon unloading; (2) plastic flow (volume-conservative) due to the involved shear stresses; and (3) structural densification (non-volume conservative) in a hemispherical region under the indent. From Vickers indentation tests carried out at different loads, the crack resistance (*CR*) is determined as a measure of the critical load, which material can withstand prior to cracking [18,19]. *CR* has been found to correlate negatively with the atomic packing fraction (APF), since the amount of densification is lower in glasses with less open space [19]. Consequently, the indentation deformation of glasses with low APF (i.e., low Poisson's ratio) such as silica is governed by densification, whereas glasses with high APF (i.e., high Poisson's ratio) exhibit deformation governed by shear plasticity [20–22]. *CR* is therefore sensitive to the glass structure, which in turn is influenced by the local bonding [23], thermal history [24], and pressure history [25]. Besides compositional and structural effects on crack initiation behavior, Lawn et al. [26] have shown that radial cracks initiate more easily with increasing water content of the surrounding atmosphere. This could be due to the increased stress corrosion at the incipient crack tip (flaws on the glass surface) as the water content increases, which leads to a lower critical stress for crack initiation and subsequently a reduction in *CR*.

The influence of fictive temperature T_f on hardness and brittleness has been reported by, for example, Smedskjaer et al. [27] and Striepe et al. [24]. Both parameters exhibit a more pronounced decrease with increasing T_f in highly connected networks. In addition, the indentation fracture toughness K_I and the crack initiation decrease with T_f due to the higher amount of densification of the more open structure [24,28,29]. In agreement with these results, studies on abraded surfaces of both soda–lime–silicate glasses [30] and silica glasses with relatively high fictive temperature show higher strength and greater fatigue resistance than the same glasses with relatively low fictive temperature [11].

Most of the prior studies regarding the influence of humidity on micromechanical properties have focused on silica glass fibers and soda–lime–silicate glasses with only two different states: low and high-fictive temperature. In this work, we investigate the influence of the atmospheric water content on the crack initiation probability of a commercial alkaline earth aluminosilicate glass, which was systematically annealed at different durations to prepare samples with a wide range of fictive temperatures (ΔT_f is in a range of 130 K). Furthermore, we show how this systematic change in T_f affects the SCCG and fatigue resistance. These glasses have previously been extensively studied with respect to the visco-elastic and other thermo physical properties [24,31–33]. To the best of our knowledge, a systematic study on the development of *CR* and K_I from dry to wet atmospheres for glasses with different fictive temperatures has not been conducted yet.

2. Experimental procedures

2.1. Glasses

The glass system under investigation is a commercial alkaline earth aluminosilicate composition with glass transition temperature T_g = 1055 K [31] used for p-Si liquid crystal display substrates [34]. Glass sheets with dimensions of approximately 25 × 25 × 0.7 mm^3 were annealed for various times t_a between 0 and 18300 min at T_a = 973 K (≈0.92 T_g) in order to obtain a wide range of fictive temperatures, as described in details elsewhere [24].

2.2. Indentation experiments

A first series of Vickers indentation tests was performed under humid conditions (*RH* = 40%, *T* = 298 K). The indents were made with a dwell time of 15 s at loads in the range between 1.96 and 19.6 N (HMV2000, Shimadzu, Kyoto, Japan) and in the range of 0.2 to 1.5 N (UNAT-M, Asmec, Radeberg, Germany), respectively. In a second series, indents at the same loads were conducted in deionized water (*T* = 298 K), which is hereafter referred to as *RH* = 100%. For observing the slow crack growth one indent per glass specimen was performed in a third series (*RH* = 30%, *T* = 298 K) at a load of 9.81 N. The relative humidity was chosen to 30% to minimize effects of crack tip condensation on SCCG [5,15,35].

For series 1 and 2, the number of initiated radial corner cracks was counted (10 indents per load) after a sit-in time of 24 h allowing subcritical crack growth and dissipating residual stresses. Wada et al. [18] showed that the number of radial cracks increases with increasing indentation load in a sigmoidal-like course. Per indent four radial cracks can be initiated in maximum, corresponding to 100% crack initiation probability. Wada et al. [18] defined the crack resistance (*CR*) as the load required producing in average two out of four radial cracks, which is equal to a crack initiation probability of 50%.

To determine the different geometrical parameters of the plastic deformation zone and the crack system, the indent diagonal length and length of radial corner cracks were measured. Therefore, five additional imprints under conditions of series 1 and 2 were performed at a load of 9.81 N. To prohibit any SCCG or stress corrosion phenomena, 3D-laser scanning microscopy measurements were performed immediately following unloading (≈20 s). From these imprints, Vickers hardness was calculated as

$$H_V = \frac{P}{2.157 \times 10^{-3} a^2} \tag{1}$$

where H_V is Vickers hardness (GPa), P is the applied load (N), and a is the half diagonal of the indent (μm).

From the obtained data of Vickers hardness H_V, Young's modulus E (from ref. [24]), crack length c, the half diagonal of the indent size a, and a geometrical factor ϕ (≈3), the stress intensity factor at the crack tip K_I was calculated using the approach of Niihara et al. [36]. We note that the applied load of 9.81 N led to crack-to-indent size ratios $c/a \geq 2.5$, which were sufficient to generate a semi-elliptical median-radial crack system (half-penny) (Fig. 1). This crack system is necessary to satisfy the conditions of the following equation for calculating K_I, when c is measured immediately following indentation [36,37],

$$K_I = 0.129\left(\frac{c}{a}\right)^{-3/2}\left(\frac{H_V\sqrt{a}}{\phi}\right)\left(\frac{H_V}{E\phi}\right)^{-2/5}. \tag{2}$$

Quinn and Bradt [38] have clearly demonstrated that in *R*-curve-dependent polycrystalline ceramics, the fracture toughness determined using the parameters obtained from Vickers indentation (K_I) does not correspond to the fracture toughness obtained using standardized tests. K_I corresponds to a single point on the *R*-curve, which is different from that of the standard tests (K_{IC}) and K_I values should therefore only be used for internal comparison. For homogeneous glasses, however, extrinsic and intrinsic microstructural toughenings behind and ahead of the crack tip are absent [39]. Thus, Vullo and Davis [40] have shown that the results obtained for glasses using the indentation method are strongly correlated with fracture toughness values measured using standard techniques. We note, that the indentation size effect (ISE) can result in an apparent higher measured toughness and lead to an erroneous rising *R*-curve. Here, we have performed the study with a constant high indentation loading force, assuming that K_I was not affected by ISE as shown in ref. [25] for borate glasses. Further we