Journal of Non-Crystalline Solids 491 (2018) 64–70

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Time and humidity dependence of indentation cracking in aluminosilicate glasses

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ARTICLE INFO

Keywords:
Oxide glass
Indentation
Crack initiation
Crack resistance
Environmental effect

ABSTRACT

The inherent brittleness and poor crack resistance of oxide glasses have always been among their main limitations for many advanced applications. As the formation of cracks leads to amplification of applied tensile stresses and ultimately catastrophic failure, there is an interest in understanding the compositional and structural dependence of crack initiation and growth. The resistance to cracking can conventionally be measured using instrumented indentation that mimics the real-life damage for certain applications. Wada introduced a method to evaluate the crack resistance by counting the number of initiated cracks as a function of the applied load. Experiments have shown that the environmental humidity and the time period between indentation and crack counting both affect the crack resistance value, but unfortunately these parameters are not always reported in literature studies. Here we perform a systematic study of the time and humidity dependence of crack initiation in calcium aluminosilicate glasses. Depending on the experimental conditions (time and humidity), the crack resistance of an aluminosilicate glass can vary by more than a factor of two. Furthermore, the observed radial/median cracks can initiate several hours after indentation. These results therefore indicate the need for a standardized procedure for determination of crack resistance to allow comparison of data from different research groups. We suggest including a sufficiently long waiting period (such as 24 h) between indentation and crack counting, as the majority of the crack initiation will then have occurred.

1. Introduction

Although they are among the manmade materials with the highest intrinsic strength [1], a major drawback of oxide glasses for many applications is their inherent brittleness [1–4]. The practical strength of glass is compromised by the presence of surface flaws, which act as stress intensifiers ultimately leading to brittle fracture since oxide glasses do not have a stable shearing mechanism to dissipate the stresses [5]. Glass scientists have attempted to decrease the risk of catastrophic failures through both compositional design and various post-treatments (e.g., thermal tempering, lamination, partial crystallization, and ion exchange) [6].

Sharp point contact is a primary failure mode for cover glasses in personal electronic devices. Since Vickers indentation can be used to replicate these failure conditions and due to its reproducibility and ease of sample preparation/measurement, it is a suitable method for evaluation of the cracking behavior of glasses for many industrial applications [7]. In Vickers indentation, a diamond pyramid with a defined pyramidal shape with the opposite faces having an angle of 136° is loaded onto the surface of a flat, polished sample. By measuring the size of the resulting indentation relative to the applied force on the sample, hardness can be obtained. The test can also be used to study the crack initiation and growth behavior of glass. Traditionally, the cracking behavior is quantified through the relationship between indentation load and crack initiation probability. The resistance to crack initiation is typically quantified using the approach of Wada et al. [8], in which crack resistance (CR) is taken as the indentation load which on average generates two radial/median cracks from the indent corners. CR can thus be viewed as a measure of the resistance to surface damage, but its determination is not straightforward. For example, indentation cracks are difficult to detect when they are located beneath the surface, aligned with the indentation edge, or too small to be observed using optical microscopy [9].

In addition to the indentation load, the chemical composition and any post-treatment of the glass [8,10] also affect the generation of cracks. Moreover, the experimental conditions, including indentation time [11,12], indenter tip geometry (including wear of the indenter tip) [13], and surrounding environment have a profound effect on the

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https://doi.org/10.1016/j.jnoncrysol.2018.04.009
Received 5 February 2018; Received in revised form 20 March 2018; Accepted 2 April 2018

cracking behavior of glasses. For example, the “less-brittle” soda-lime-silica glass of Sehgal and Ito features a crack resistance of 3.5 kgf when measured in pure nitrogen atmosphere [14], but only 1.0 kgf when measured in air [15]. The origin of the relation between crack initiation and atmospheric humidity is not fully elucidated in literature, but the possible mechanisms responsible for water-assisted crack initiation could be related to a reaction between gaseous water and strained Si—O bonds in the indent [16,17]:

$$\equiv Si–O–S\equiv + H_2O \rightarrow 2\equiv SiOH$$

This is the idealized reaction for pure silica glass, but a similar hydrolysis reaction has been reported for Al—O bonds [16]. An introduction of modifiers such as alkali or alkaline-earth cations yields dangling bonds in the glass structure, which can facilitate a more rapid hydrolysis reaction. Moreover, the hydrolysis reaction rate is reported to increase when the glass is under compressive stress [18], probably due to the energetically unfavorable strained bonds. An alternative explanation relates to the entrance of water into the glass during indentation, resulting in a weakening of the glass structure [19–21], which has been reported, e.g., as reduced elastic moduli [18]. Water does not significantly enter most silicate glasses at room temperature due to a low diffusion rate; hence the proposal of a stress-assisted entry [19]. Water entry has been reported to be the cause of low crack resistance [17].

The influence of water vapor on other glass mechanical properties has been thoroughly described, including the influence of water vapor on crack propagation [3,22,23] and glass fatigue [2,4,24]. The influence of liquid water on crack initiation has also been reported [20], although most literature studies have investigated the effect of water on pre-existing cracks. Striepe et al. [24] showed that water vapor increases the crack initiation probability, with the largest change for dense glasses with lower fictive temperature. Despite the reported dependence of crack initiation on humidity, there is no standard testing procedure for determining CR in the literature. From a set of 32 papers on indentation crack resistance of oxide glasses [15,24,26–55], approximately half of the studies reported the atmospheric conditions or immersion medium, while the rest contained either no information about the humidity or merely stated that the experiment was conducted under “ambient conditions” (Fig. 1). However, this information is insufficient, since ambient conditions can cover relative humidity (RH) values down to ~30% in the winter and up to ~80% in the summer in our laboratory in northern Europe. Furthermore, Lawn et al. [25] investigated crack initiation for soda-lime silicate glasses as a function of contact time and atmospheric environment, observing delayed cracking up to 600 s after unloading of the indenter. That is, the time period between indent imprinting and crack counting also influences the determined crack resistance, as cracks can initiate over time, presumably due the kinetics of stress-corrosion hydrolysis.

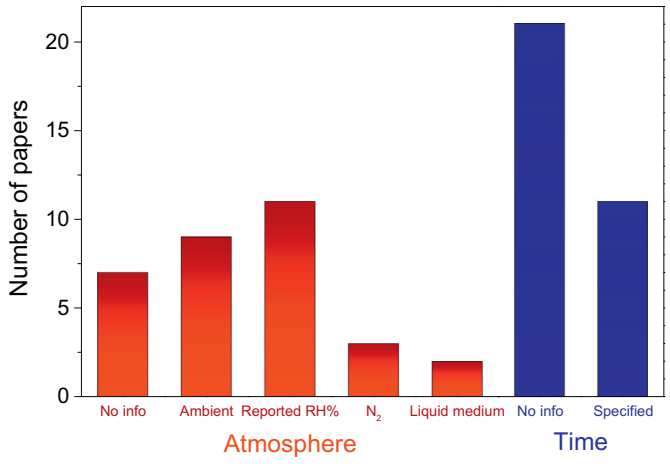

Fig. 1. Summary of the experimental conditions reported in literature studies used when determining crack resistance, including the atmospheric conditions and the time between indentation and counting of the number of cracks. Although not always adequately described, the atmospheric conditions are more often reported than the time between indentation and crack counting. The data have been obtained from Refs. [15, 24, 26–55]. The data were found among the papers referring to Wada's original work, using combinations of the keywords “crack”, “crack resistance”, and “crack initiation” for oxide glasses.

In the aforementioned set of 32 papers, approximately one third specify the period between indent imprinting and crack counting (Fig. 1), with no explicit reasoning given for the choice and inclusion of short waiting periods (< 30 s) to allow fast data collection or long waiting periods (24 h). To our knowledge, only the paper by Scannell et al. [36] has recently investigated the time dependence of crack initiation, as they reported that crack initiation ceased two hours after indentation for soda-titania-silicate glasses [36]. The dwell time during indentation, which is the time the indenter is held at maximum load, is 15 s in two-thirds of these 32 papers. Dwell time has been shown to affect glass hardness [11,12,20], but to the best of our knowledge, the relationship between crack initiation and dwell time has not been reported in the literature. No reason is given for the choice of dwell time in any of the 32 papers. We note that the recommended dwell time for Vickers hardness measurements is 10–15 s according to ASTM E384 [56], which could be the reason for the common use of 15 s dwell time in crack resistance measurements.

In this work, we investigate the combined humidity and time dependence of crack initiation to improve the understanding of stress-release and cracking behavior of oxide glasses and develop an experimental testing protocol for determining the crack resistance. We evaluate the time dependence by continuously monitoring the crack initiation for at least 6 h following indentation, enabling accurate determination of the time of crack initiation. As in most laboratories, the indenter instrument is not placed under a controlled atmosphere, and we therefore evaluate the humidity dependence of indentation cracking by performing the experiments during winter (relative humidity of 39 ± 8%) and summer (relative humidity of 70 ± 9%). The experiments are performed on two calcium aluminosilicate glasses (one tectosilicate and one peralkaline composition).

2. Experimental section

The synthesis of the tectosilicate $60.3SiO_2$–$19.7Al_2O_3$–19.6CaO and peralkaline $66.9SiO_2$–$12.3Al_2O_3$–20.3CaO (measured compositions, in mol%) glasses was done using the melt-quench procedure, as described in detail elsewhere [57]. The quenched glasses were cut and ground to an optical finish before being annealing for 30 min at their respective glass transition temperature T_g of 1092 and 1129 K, as previously reported in Ref. [57]. The glasses were named according to their nominal Al_2O_3 content, i.e., Al20 and Al12. Using an ultrasonic thickness gauge, Young's modulus and Poisson's ratio were determined to be 91 ± 1 GPa and 0.25 ± 0.01, respectively, for Al20 and 83 ± 2 GPa and 0.25 ± 0.01, respectively, for Al12.

The crack initiation probability was measured using a Vickers microindenter (Duramin 5, Struers A/S) in air at 22–24 °C. Only radial/median cracking from the corners of the indents was observed in these glasses. The indents were performed at loads of 0.49, 0.98, 1.96, 2.94, 4.91, and 9.81 N using a dwell time of 15 s. Images of the indents were collected using optical microscopy every 10 s for the first 2–3 h after the initial indentation and every 5 min for up to 6–8 h after indentation (Fig. 2). We set $t = 0$ at the end of the 15 s dwell time, when the indenter pyramid starts to unload. The first observation is made at $t = 15$ s, as this is the time needed for turning from indenter to camera mode on our instrument. The setup allows us to accurately determine the time at which indentation cracking occurs, as exemplified in Fig. 3. In this case, no cracks were visible immediately following unloading of the indenter, but after 343 s the first crack appears, followed by three