Journal of Non-Crystalline Solids 494 (2018) 13–20

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

# Crack-resistant glass with high shear band density

T.M. Gross*, J. Wu, D.E. Baker, J.J. Price, R. Yongsunthon

*Corning Research and Development Corporation, Sullivan Park, Corning, NY 14831, United States.*

ARTICLE INFO

*Keywords:*
Indentation
Shear
Densification

ABSTRACT

The contact deformation mechanisms were explored for a series of 15CaO $15Al_2O_3$ $xB_2O_3$ (70-x)$SiO_2$ glasses exhibiting intermediate indentation behavior. These glasses are defined as intermediate since they deform with significantly higher densification than the comparative normal glass, soda-lime silicate, and significantly more shear deformation that the comparative anomalous glass, Corning 7980 fused silica. Berkovich scratch testing at 30 mN shows that 50% of the scratch impression area is displaced into the pileup region for the normal soda-lime silicate glass, while only 9% of the scratch impression area is displaced into the pileup region for anomalous silica glass. For the series of intermediate glasses studied from x = 5 to x = 25, the scratch area displaced into the pileup region was constant within measurement error at approximately 30%. Since the displaced volume indicates the amount of shear deformation, the relative amounts of shear and densification are considered constant across the intermediate glass series. However, the indentation cracking thresholds are significantly different for the intermediate glasses with the x = 25 endpoint requiring a 3 kgf load to produce median/radial cracks, whereas the x = 5 endpoint glass required only 1 kgf to produce median/radial cracks. A cross-sectional view of the x = 25 glass shows that that deformation occurs with high shear band density, however, these shear bands have not progressed into shear faults. The shear band density and crack resistance both increase as the $B_2O_3$ content increases for the 15CaO $15Al_2O_3$ $xB_2O_3$ (70-x)$SiO_2$ glass series.

## 1. Introduction

Glasses can be categorized by the Vickers indentation deformation response as normal, intermediate, or anomalous [1]. At one extreme are normal glasses such as soda-lime silicate that deform to a large extent by volume displacing shear [1–5]. These glasses contain an abundance of non-bridging oxygens (NBOs) that provide pathways through weaker ionic bonds where shear faulting readily occurs [5]. The alignment of NBOs into pathways has been described by the modified random network model [6]. The shear faults act as starter cracks for larger indentation cracking systems, i.e. median/radial and lateral cracks, at modest loads [3,4]. At the other extreme are anomalous glasses such as fused silica that deform primarily by volume reducing densification [7–9]. These glasses have few NBOs and high free volume, but also have a highly constrained glass network since nearly all of the tetrahedra are connected at all four corners. This highly connected network is resistant to shear deformation, but results in high surface tensile stresses around the periphery of the contact and at the bottom of the elastic/plastic boundary [10]. The surface tensile stresses around the periphery of the contact will act upon surface flaws to form a ring crack whereas the tensile stresses at the bottom of the elastic/plastic boundary promote median cracking. In between normal and anomalous glasses is a third subset described as intermediate glasses. These glasses are called intermediate since deformation occurs with significantly more densification than normal glass and significantly more shear than anomalous glass [1]. These glasses also have minimal NBOs, so are resistant to shear faulting when compared to normal glass. The network connectivity of these glasses is lower than anomalous glass such as fused silica by incorporation of trigonally coordinated boron structural units. The reduced connectivity allows greater shear deformation when compared to anomalous glasses, so that the intermediate glasses are given relief from the stresses that form ring and median cracks [10].

During diamond indentation, shear deformation occurs along shear bands [1–5]. A shear band is a localized plastic deformation occurring in a narrow zone of excessive strain. The extreme localization of deformation along a shear band is such that it precedes fracture. In the case of normal glass, shear bands readily progress into shear faults since the deformation occurs along aligned weak ionic bonds associated with NBOs [5,6]. It is demonstrated in the current research that glasses can be designed that deform with significant shear band density, yet are resistant to the formation of faults along these shear bands.

The Vickers indentation thresholds of the 15CaO $15Al_2O_3$ $xB_2O_3$ (70-x)$SiO_2$ (CABS) series were previously reported and indicated that the crack resistance increased as $B_2O_3$ was substituted for $SiO_2$ [11].

* Corresponding author.
*E-mail address:* grosstm@corning.com (T.M. Gross).

https://doi.org/10.1016/j.jnoncrysol.2018.04.048
Received 23 March 2018; Received in revised form 19 April 2018; Accepted 25 April 2018

The improved crack resistance of the high $B_2O_3$ glass was attributed to a reduction in constraints as trigonal units were substituted for tetrahedral units. It was suggested that the reduction in constraints can then allow for structural rearrangements to take place more readily during indentation deformation, but the deformation mechanism was not determined. Recently, bulk densification studies on this glass series reveal that the high boron endpoint glass will densify to the largest extent, however, the difference in relative densification between the high silica endpoint glass and the high boron endpoint glass was only 3% [12]. If the ability to densify is also relatively constant for indentation deformation across this series, the mechanism of the shear deformation component may have a significant impact on the crack resistance. The CABS system is further explored in this current work to understand the deformation mechanisms that lead to the high crack resistance of the high $B_2O_3$ endpoint glass.

## 2. Experimental

The CABS glasses were prepared from Baolin sand, calcined alumina, technical grade boric acid, and Franklin limestone. A generic soda-lime silicate glass was also prepared using the same raw materials as well as sodium carbonate, potassium carbonate, and magnesium oxide. The raw materials were mixed in a Turbula mixer then melted for 12 h at 1650 °C in covered Pt crucibles. The molten glasses were then poured onto a clean stainless steel table and transferred to annealing furnaces set to estimated anneal points for each glass. Glasses were annealed for 6 h and then furnace cooled to room temperature at a cooling rate of 100 °C/h. Table 1 gives the analyzed compositions. $SiO_2$, $Al_2O_3$, $Na_2O$, $K_2O$, MgO, and CaO contents were determined using x-ray fluorescence and $B_2O_3$ content was determined using inductively coupled plasma optical emission spectroscopy. The density was determined by buoyancy method and anneal and strain points were determined by beam bending viscosity. Silica glass, Corning Code 7980, was also obtained for study. Test specimens for each glass were prepared in dimensions of 25 mm × 25 mm × 1 mm. The flats were polished to an optical finish. Following sample preparation, the glasses produced by crucible melting were re-annealed at their respective measured anneal points for 4 h to set the fictive temperatures equal to the anneal point temperatures.

Scratches were made in test specimens with a Berkovich tip at a constant load of 30 mN using a MTS Nano G200 nanoindenter. The 30 mN load was selected since higher loads produced significant machine curling of pile-up material, thus making subsequent pile-up measurements difficult. The scratch impression area and pile-up areas were measured using atomic force microscopy (AFM). The AFM scans were performed on a Bruker Bioscope Catalyst in tapping mode using TESP probes. The substrates were manually positioned such that the scratches were perpendicular to the fast scan (horizontal) axis, to ensure that any tip geometric convolution effects would be consistent across all samples. Slow scan rates, low feedback gains, and moderate tapping setpoints were used to minimize “overshoot” artifacts at the pileup regions and optimize topographic accuracy. The scratches were centered relative to the scan region and the scans were flattened with a second order polynomial fit to flat (control) regions on both sides of the scratches. Matlab was used to calculate the scratch and pileup areas for every scan line (row) of the 512 × 512 pixel height images. The averages were calculated from values extracted across all rows in an image, only excluding anomalous scan lines. The uncertainties quoted for all extracted parameters represent true variability of the calculated areas, not instrumental error. The variability of the area calculations is mostly due to real variability of the scratch topography, however, some of it can be attributed to polishing flaws on the substrate surfaces.

Cross-sections of 1 kgf Vickers indents were prepared by the method described by Hagan [4,9]. A Leco LV800AT Vickers hardness tester was used to make the indents at the tip of a pre-existing crack. One major diagonal of the indent impression was aligned with the pre-existing crack, so when fracturing the sample, the indents would be bisected into two halves for analysis. One half of the indentation was analyzed in the as-received condition without etching, the other half of the indentation was lightly acid etched to enhance surface topography associated with shearing. Etching was done in a 0.1% HF solution for 30 s followed immediately by a DI water rinse to remove precipitates from the etching solution. The samples were then coated with conductive carbon to reduce charging. The samples were analyzed using a Zeiss 1550VP FESEM operated at 5 kV accelerating potential and at a beam current of approximately 150 p-Amps. The lower beam energy decreases the landing energy of the analysis beam, enhancing surface sensitivity. Secondary electron images were acquired using the Everhart Thornley secondary electron detector as its off-axis geometry relative to the sample surface helped with observation of surface topography associated with shearing.

## 3. Results

The AFM line scans taken perpendicular to the scratch direction for the 30 mN Berkovich scratches are given in Fig. 1 for the soda-lime silicate, the CABS glasses, and fused silica. As shown in the image overlays, the pile-up region does exhibit a small degree of machine curling for several of the glasses. At higher scratch loads, the propensity towards formation of machine curls increases. Fig. 2 shows an example of an elongated machine curl produced in CABS15 at 160 mN. As shown in Fig. 3, AFM line scans clearly indicate that the machine curl is a detached segment of the pile-up region, so machine curl regions had to be carefully avoided in performing pile-up measurements in order to

**Table 1**
Glass compositions and packing calculations.

| Analyzed Compositions (mol%) | Soda -lime silicate | CABS5 | CABS15 | CABS25 | $SiO_2$ |
|---|---|---|---|---|---|
| $SiO_2$ | 70.92 | 64.68 | 55.63 | 46.09 | 100 |
| $Al_2O_3$ | 1.06 | 15.09 | 14.82 | 15.04 | |
| $B_2O_3$ | | 4.94 | 14.48 | 23.5 | |
| $Na_2O$ | 12.71 | | | | |
| $K_2O$ | 0.21 | | | | |
| MgO | 5.84 | | | | |
| CaO | 9.26 | 15.29 | 15.07 | 15.38 | |
| Glass type | Normal | Intermediate | Intermediate | Intermediate | Anomalous |
| Anneal Pt. (°C) | 553 | 793 | 707 | 664 | 1180 |
| Density (g/cm3) | 2.469 | 2.497 | 2.45 | 2.419 | 2.2 |
| Molar volume ($cm^3$/mol) | 24.03 | 26.54 | 27.38 | 28.12 | 27.31 |
| oxygen atoms/$cm^3$ | 4.34E + 22 | 4.65E + 22 | 4.71E + 22 | 4.78E + 22 | 4.41E + 22 |
| total atoms/$cm^3$ | 7.19E + 22 | 7.37E + 22 | 7.56E + 22 | 7.75E + 22 | 6.61E + 22 |
| oxygen packing density | 0.409 | 0.467 | 0.455 | 0.446 | 0.412 |
| total packing density | 0.450 | 0.480 | 0.465 | 0.455 | 0.413 |