Journal of Non-Crystalline Solids 355 (2009) 563–568

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

A glass with high crack initiation load: Role of fictive temperature-independent mechanical properties

T.M. Gross [1], M. Tomozawa *, A. Koike [2]

Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York 12180-3593, United States

ARTICLE INFO

Article history:
Received 21 November 2008
Available online 5 March 2009

PACS:
62.20.Qp
62.20.Mk
81.05.Kf
81.70.Bt
81.70.Cv

Keywords:
Glasses
Mechanical properties
Fracture
Indentation, microindentation
Oxide glasses
Silicates

ABSTRACT

The crack initiation load of a series of calcium aluminosilicate glasses and selected commercial glasses were evaluated using Vickers indentation. The results showed that a calcium aluminosilicate glass containing 80 mol% SiO_2, 10 mol% Al_2O_3 and 10 mol% CaO exhibited a high crack initiation load comparable to that of the less-brittle glass (LB glass) developed by Asahi Glass Co., Ltd. It has previously been determined that glasses experience a fictive temperature increase by indentation. The indented region of a glass, therefore, acquires, in general, different mechanical properties, such as hardness and elastic moduli, from the original, unindented glass. The extent of these mechanical property changes depends upon the glass composition and a certain glass composition with fictive temperature-independent mechanical properties can have the deformed region with matching mechanical properties to those of the undeformed region of the glass. It was found that the calcium aluminosilicate glass having no fictive temperature dependence on elastic moduli gave the highest crack initiation load. However, this composition did not coincide with fictive temperature-independence of hardness or density.

1. Introduction

Lightweight glass is in high demand for a variety of applications such as liquid crystal display (LCD) glass. The reduction of weight is typically accomplished by reduction in thickness, which requires the glass to have a higher mechanical strength. The presence of surface cracks can have a catastrophic effect and lower the strength to just a fraction of the intrinsic strength of the glass. Glasses with a greater resistance to cracking by contact load need to be developed and fully understood to alleviate this problem.

Recently, a special type of glass has been prepared by Asahi Glass Co., Ltd. that displays superior resistance to crack formation under an applied indentation load [1–4]. This glass is referred to as less-brittle glass (LB glass). Sehgal and Ito [1] evaluated various glasses using the brittleness parameter, H/K_c, suggested by Lawn and Marshall [5], where H is the indentation hardness and K_c is the fracture toughness determined by indentation and found that glasses with the smaller brittleness exhibited the greater crack initiation load. The fracture toughness determined by indentation, K_c, is often found different from the fracture toughness, K_{Ic}, determined from the crack growth. In Table 1, hardness, fracture toughness and brittleness [2] are compared for three glasses, commercial soda–lime silicate glass, Asahi LB glass and silica glass. It can be seen that Asahi LB glass, which exhibits a greater resistance to crack formation, has a low brittleness value as was pointed out by Ito [2]. However, when the fracture toughness values obtained from crack growth [6,7] are used instead of those by indentation, the values of H/K_{Ic} become nearly same for these three glasses. Correspondingly, the K_c value is much larger than the K_{Ic} value only for the LB glass. It appears that the origin of the less-brittleness of Asahi LB glass is related to its anomalously high value of K_c compared with its K_{Ic} value. The high value of K_c corresponds to a small crack length produced by the indentation while the greater crack resistance by indentation corresponds to the greater difficulty to form a crack and both quantities appear closely related. We seek to find the cause of the greater resistance to crack formation of glasses by examining fictive temperature dependence of mechanical properties.

Ito had previously predicted that the minimum in brittleness or the maximum of crack initiation resistance would occur in the region where silicate glasses change from normal to anomalous behavior [3]. Traditionally, normal and anomalous characteristics are defined by the temperature and pressure dependence of the elastic modulus [8]. Alternatively, one can classify the glasses by

---

* Corresponding author. Tel.: +1 518 276 6659; fax: +1 518 276 8554.
E-mail address: tomozm@rpi.edu (M. Tomozawa).

[1] Present address: Corning Inc., Corning, New York.

[2] Present address: Asahi Glass Co., Yokoham, Japan.

0022-3093/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.jnoncrysol.2009.01.022

Table 1
Hardness and fracture toughness of soda–lime silicate glass, Asahi less-brittle (LB) glass and silica glass.

	Soda–lime silicate glass	Asahi less-brittle glass	Silica glass	References
Hardness, H (GPa)	5.4	4.7	6.2	[2]
K_c (MPa m$^{1/2}$)	0.76	0.96	0.70	[2]
Brittleness, H/K_c (μm$^{-1/2}$)	7.1	5.1	9.0	[2]
K_{Ic} (MPa m$^{1/2}$)	0.70	0.65	0.80	[6,7]
H/K_{Ic} (μm$^{-1/2}$)	7.7	7.2	7.8	

their fictive temperature dependence of various properties. Soda–lime silicate glass, a typical normal glass, has opposite fictive temperature dependence of many glass properties to that of silica glass, a typical anomalous glass. A normal glass exhibits decreasing density, hardness, and elastic modulus with increasing fictive temperature. An anomalous glass exhibits the opposite trend in these properties, increasing density, hardness, and elastic modulus with increasing fictive temperature. Intermediate glasses will show fictive temperature-independence of these properties.

It has been shown that the fictive temperature in the region surrounding a Vickers indentation experiences a deformation-induced fictive temperature increase [9,10] which, in turn, changes glass properties such as density, hardness, and the elastic modulus. Therefore, it is reasonable to expect that the propensity to initiate a crack under an indentation may be related to the fictive temperature dependence of mechanical properties such as hardness and elastic modulus, with greater change of these properties with fictive temperature leading to easier cracking. In fact, we have shown recently that one of the indentation-related properties, indentation size effect of the hardness, becomes minimum for the glass with the smallest hardness change with fictive temperature [11].

A series of calcium aluminosilicate glasses with various silica contents, the same glasses used for the indentation size effect study [11], were used to investigate the crack initiation loads using Vickers indentation. The result was compared with fictive temperature dependence of mechanical properties such as hardness and elastic modulus.

2. Experimental

Calcium aluminosilicate glasses, $(100 - x)(\mathrm{CaO} \cdot \mathrm{Al_2O_3}) - x\mathrm{SiO_2}$, with x ranging from 60 to 100 mol% (all percentages will be given in mol% unless otherwise stated) were prepared from sol–gel derived silica, reagent grade alumina, and reagent grade calcium carbonate powders. Compositions were chosen to contain equal mole percents of alumina and calcia and are expected to have no non-bridging oxygen. The high purity SiO_2, Al_2O_3 and $CaCO_3$ powders were melted in a zirconia-dispersed 90% platinum-10% rhodium crucible of 60 cc capacity at temperatures ranging from 1700 to 1800 °C. The glass melt along with the crucible was quenched in cold water to form an annular crack for removal of the glass. Non-porous glasses with SiO_2 content from 60% up to 90% could be prepared by melting in the crucible at temperatures up to 1800 °C. Glasses with silica contents exceeding 90% were unconventionally prepared using the Gleeble 1500 instrument manufactured by Dynamic Systems, Inc. These glasses contained a high amount of porosity after melting at 1800 °C in the crucible and a higher temperature of approximately 2000 °C was obtained by the use of the Gleeble. The Gleeble is a welding research instrument that can be set up to pass a high current through a graphite heating rod. A 0.5 inch hole was drilled in the graphite rod into which the porous glass sample was placed. The sample was then heated under vacuum conditions by a.c. electric current through the rod. The melted sample was then removed and the surface layer which contained some carbon contamination was polished away to reveal a non-porous sample. After melting, all the prepared calcium aluminosilicate glasses were rough annealed at $T_g + 100$ °C and furnace cooled. Commercial glasses including Asahi LB glass, BK7, NBS 710, synthetic silica glass (Asahi AQ, OH = 50 ppm), GeO_2-doped silica glass, and Vycor® (Code 7913) were also obtained for study.

To study crack initiation, glass samples were cut to approximate dimensions of 5 × 5 × 2 mm using a diamond saw. One 5 × 5 mm face was polished using 240, 400, 600, and 800 grit SiC paper followed by polishing to an optical finish using cerium oxide slurry. The cut and polished samples were then heat-treated at T_g for 4 h minimum in dry N_2 atmosphere and then allowed to furnace cool to prevent residual surface stress. Crack initiation tests were performed by indentation of the glass samples using a Leco M-400 microhardness tester equipped with a Vickers indenter. Since moisture in the atmosphere promotes crack formation, the hardness tester was enclosed in a glove bag in a dry nitrogen atmosphere. The glove bag was evacuated and filled with nitrogen then re-evacuated and re-filled with nitrogen prior to testing. A small positive pressure of nitrogen was maintained to prevent atmospheric air from entering in the case that small leaks may be present in the glove bag. Samples were immersed in dry toluene prior to placing in the glove bag then removed under the nitrogen atmosphere and wiped dry before testing. Toluene is a non-polar solvent with very low water solubility [12].

The crack initiation load is defined in this work as the load required to create two out of four possible cracks stemming from the corners of the diamond shaped indentation [1,13–15]. For the anomalous glasses, such as silica and GeO_2-doped silica glasses, the conical cracks connecting adjacent corners were counted, taking a conical crack in a quadrant as one crack, with a maximum of four cracks when all four quadrants contained conical cracks. Loads of 25, 50, 100, 200, 300, 500, and 1000 grams force (gf) were applied to each sample. Ten indentations were made at each load and the number of cracks was recorded for each indentation. The average number of cracks per indentation was plotted versus the load and sigmoidal curves were used to fit the data within experimental error. The error in the load required to form 2 cracks on average is then determined with the possible range in load values from the sigmoidal curves.

The dependences of various mechanical properties on fictive temperature, T_f, were then determined to see if they relate to the crack initiation load for a given glass. To determine the hardness dependence on fictive temperature, samples of each glass were heat-treated at four different temperatures near T_g for sufficient periods of time to produce samples with four different fictive temperatures. The sufficiency of heat-treatment times for these glasses has been verified experimentally in previous work by monitoring the structural relaxation with time by density measurement [11].

Hardness was determined as a function of fictive temperature by taking ten 100 gf indentations at each of four different fictive temperatures for each glass sample studied. Prior to heat-treatment, the indentation surface was polished in the same manner as the crack initiation samples. The sample size was also 5 × 5 × 2 mm. This test was again performed under a dry nitrogen environment since hardness is known to depend on loading time when testing is performed under atmospheric air [12]. The indentation load of 100 gf was used to show the dependence of hardness on fictive temperature because this load gave little, if any, cracking for the glasses studied. This allowed for accurate measurement of hardness. However, due to the indentation size effect, higher loads will give lower hardness values [12,16–18]. The indentation size effect is defined as the load dependence of hardness, where at