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Elastic properties and indentation cracking behavior of Na_2O-TiO_2-SiO_2 glasses

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ABSTRACT

The effects of composition on indentation deformation and cracking behavior of Na_2O-TiO_2-SiO_2 glasses were studied in the light of structural considerations and parameters such as the atomic packing density (C_g) and the network energy, using a combination of elastic measurements and micro-hardness indentation experiments. Na_2O-TiO_2-SiO_2 glasses with titania contents of 4–10 mol% and sodium oxide contents of 10–25 mol% were prepared through a traditional melt-quench process. Indentation experiments were conducted using a Vickers indenter with loads ranging from 10 mN to 49 N. Critical loads for crack initiation and cracking patterns were systematically investigated and correlated with the elastic properties of glass. In this ternary system concerning a relatively large range of Poisson's ratio (ν), a minimum in critical crack initiation load was observed at a ν of 0.21–0.22. This study brings to light the unusual role of titanium in the glass network, which gives birth to peculiar trends in the structural and mechanical properties.

1. Introduction

An intriguing correlation was observed recently in oxide glasses and in metallic glasses: the fracture energy (G) increases with the Poisson's ratio (ν), with a sharp brittle-to-ductile (BTD) transition at a critical $\nu_{BTD} = 0.31$–0.32 [1]. A similar Poisson's ratio-ductility correlation has also been reported in crystalline metals [2]. Recently, Rouxel also showed that densified silica, when ν increases from 0.15 to 0.25, is capable of shear flow under indentation resulting in pile-ups [3] and found that ν is directly correlated with the atomic packing density (C_g) and the glass network dimensionality [4]. Such a far-from-equilibrium fracture property versus near-equilibrium elastic property relation is quite unexpected, yet highly beneficial by setting ν as an optimization target to make stronger and tougher glasses. The precise measurement of fracture toughness and the associated fracture energy requires large samples and tedious sample preparation. However, elastic characteristics, especially Poisson's ratio can be measured relatively easily, using much smaller samples, such as mm sized samples for ultrasonic measurements and tens of μm sized samples for Brillouin light scattering experiments. In both methods, ν can be easily calculated from the measured longitudinal (V_L) and transverse (V_T)sound velocities: $\nu = (V_L^2 - 2V_T^2)/[2(V_L^2 - V_T^2)]$. The ν-G relation has already been proposed as a guide to obtain tough metallic glasses [5,6]. It is of great scientific and technological interest to investigate whether a similar relation holds in oxide glasses, as stronger and tougher glasses are increasingly demanded for applications such as personal electronics, windows for transportation systems, architectural materials, solar panels, and submarine communications cables, etc.

Indentation is a relatively simple way to observe the mechanical behavior of glass and the initiation of cracks under contact loading. Wada et al. described the susceptibility to cracking in a glass by its crack resistance, or the critical load to initiate two cracks from a Vickers indentation [7]. Sehgal and Ito [8] used a "brittleness" index, proposed by Lawn and Marshall as a ratio of hardness to fracture toughness [9], as a measure of glass resistance toward cracking. However, it is unclear whether this relationship is sufficiently refined to allow for the comparison of glasses with slight changes in composition. Additionally, Kato et al. showed that the crack resistance does not have a clear relationship with either Vickers hardness or the fracture toughness [10]. It seems that to predict the cracking behavior of glass under indentation, the effects of permanent deformation during indentation (densification and shear flow) on the stress field need to be better understood. At lower ν, the primary mode of deformation under indentation is densification, as ν increases, a shift from densification to shear flow is expected [3]. This shift is accompanied by a change in the cracking behavior [11].

In this work, we examine whether relationships between the mechanical properties measured through indentation and the ν exist by focusing on soda-titania-silicate glasses covering a range of ν from 0.18 to 0.24. The Na_2O-TiO_2-SiO_2 glass system was chosen because it covered a large range of Poisson's ratio, both Na_2O and TiO_2 are known to separately cause unusual behavior in silicate glasses (anomalous elastic

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moduli behavior with respect to temperature and anomalous thermal expansion respectively).

To understand the elastic properties and the indentation behaviors of glass, it is important to consider the glasses from a structural standpoint. The basic bonding environment of Si and Na is fairly well known, with Si forming tetrahedrally coordinated with four oxygen atoms and Na breaking a Si-O-Si bond to form a nonbridging oxygen, Si-O-Na. The basic bonding environment of Ti is more complicated, being able to adopt four, five, or six-fold coordinations, depending on the concentration and species of the other cations present in the glass. Farges et al. found that in Na_2O-TiO_2-SiO_2 glasses, Ti primarily adopts a fivefold coordination with a square pyramidal geometry, with four bridging oxygens and one double bonded nonbridging oxygen [12,13]. The effect of TiO_2 on the mechanical properties and the structure of glasses depends strongly on its coordination state, and is still poorly understood.

2. Experimental details

Soda-titania-silicate glasses were synthesized through a traditional melt-quench method from powders. Glasses with compositions of (x)Na_2O-(y)TiO_2-(1-x-y)SiO_2, where x = 10, 15, 20, and 25 and y = 4, 7, and 10 mol%, were chosen to cover a range of Poisson's ratios ($\nu = 0.18$–0.24). Powders used were of 99% purity or higher. Powders were mixed for approximately 30 min and then melted in a Pt or a 10%Rh-90%Pt crucible at 1400–1500 °C for three hours, with the powder added in three to four intervals during the first hour. The temperature was increased to 1600–1700 °C for ten minutes prior to quenching to make pouring the glass easier. After pouring, the glasses were quickly transferred into an annealing furnace set slightly above their glass transition temperatures (550–600 °C) for 1–2 h and furnace cooled overnight. Glasses were visually checked for residual stresses using a polarizer and re-melted if excessive residual stresses were observed.

For indentation experiments, samples of approximately 10 mm × 10 mm × 4 mm were prepared. Samples were cut using a diamond saw and two parallel faces were polished with 240, 400, and 600 grit Al_2O_3 paper followed by a cerium oxide slurry.

Vickers indents were made using a Matsuzawa hardness indenter at 49 N, 9.8 N, 4.9 N, and 2.9 N and using a Fischer indenter at 1 N, 0.5 N, and 0.1 N. Ten indents were made at each load and images of each indent were taken using either an Olympus BX60 optical microscope or a scanning electron microscope (SEM) for indents made with the Matsuzawa and the Fischer indention machine, respectively. Apparent surface roughness/scratches in some of the images is due to residual organics from temporary storage in soft plastic containers, which was removed with alcohol/acetone after the problem was observed in initial samples. All indentations were done in air, cracking patterns surrounding indents were studied after crack growth had stopped. To determine when crack growth had stopped, images of indents across four compositions (x = 10, 15, 20, 25 and y = 4) were taken at 5 images/s for up to 24 h. Crack growth stopped and no new cracks appeared after two hours for all compositions. Fig. 1 shows the crack growth around a 1 kg indent in a 15Na_2O-4TiO_2-81SiO_2 glass over a 20 h period. In order to compare the behavior of glasses with different compositions regardless of environmental fatigue effects, it was decided to investigate the indentation patterns at least two hours after indentation.

For each indent, the number of primary cracks, secondary cracks, and circular cracks around the indent were counted. Primary cracks are defined as cracks originating from the corners of the Vickers indent and secondary cracks are cracks originating from one of the sides of the indent. The crack lengths and indent diagonals were measured under an optical microscope. Vickers hardness, and the average primary crack length were calculated. For indents made with the Fischer indenter, the loading/unloading curve for each indent was collected. The loading/unloading curves show the applied load (mN) versus indentation depth (μm) over the entire indentation cycle. From these curves the energies associated with the reversible and irreversible deformation components of the indentation process were calculated by integrating the areas underneath the curve. Reversible energy is the area under the unloading curve, while irreversible energy is the area under the loading curve minus the area under the unloading curve.

To study how the indentation behaviors change relative to the elastic properties of the glass, the transverse and longitudinal sound velocity were measured for each composition by ultrasonic pulse-echo technique using piezoelectric transducers (10 MHz range) and by

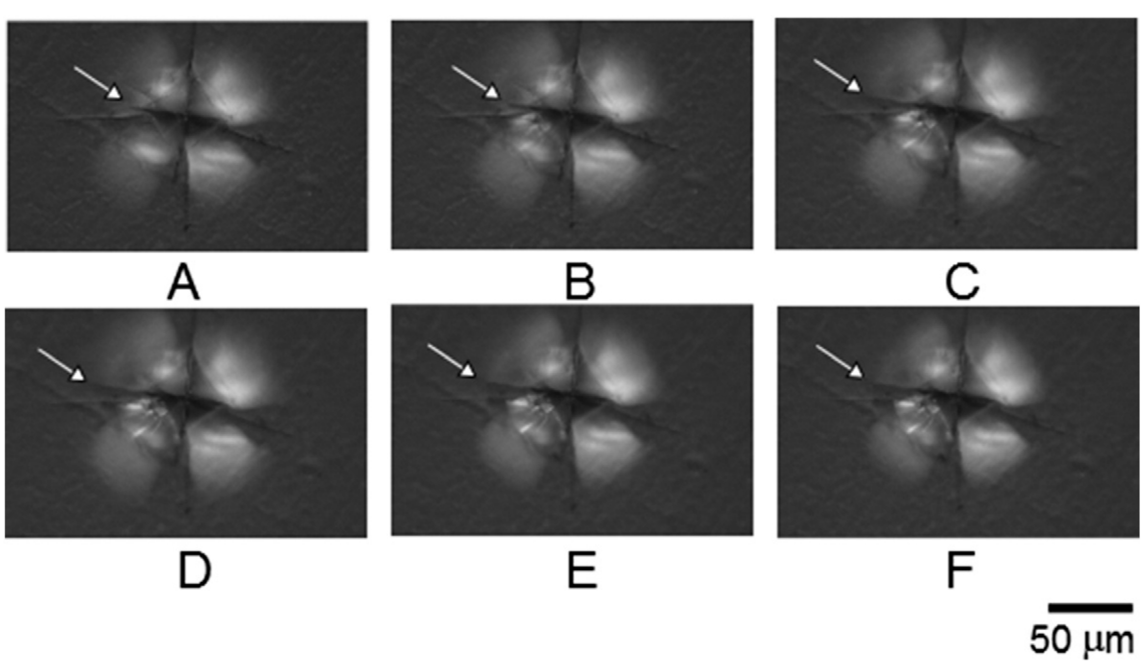

Fig. 1. Optical microscope images showing crack growth around a 1 kg Vickers indent in a 15Na_2O-4TiO_2-81SiO_2 glass at 5 min (A), 30 min (B), 1 h (C), 2 h (D), 10 h (E), and 20 h (F). Crack growth is significant over the first hour, slight over the second, and non-existent over the next 18 h. This can be most clearly seen by following the crack growth from the left-most corner of the indent (white arrows).