From network depolymerization to stress corrosion cracking in sodium-borosilicate glasses: Effect of the chemical composition

Marina Barlet [a], Jean-Marc Delaye [b], Bruno Boizot [c], Daniel Bonamy [a], Richard Caraballo [b], Sylvain Peuget [b], Cindy L. Rountree [a],*

[a] SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France
[b] CEA, DEN, DTCD, SECM, LMPA Marcoule, France
[c] LSI, Ecole Polytechnique, CEA, CNRS, Université Paris-Saclay, 91128 Palaiseau, France

ARTICLE INFO

ABSTRACT

The study herein examines how chemical composition impacts sub-critical stress corrosion cracking (SCC) in sodium borosilicate glasses. The crack speed versus stress intensity factor (v vs. K_I) curves were obtained for seven ternary SiO_2-Na_2O-B_2O_3 (SBN) glasses of selected chemical compositions. Na_2O plays an interesting role in the SCC behavior. First, increasing the Na_2O concentration yields an increase in the environmental limit (K_e). Second, increasing the Na_2O concentration affects how fast SCC occurs as K_I increases (i.e. the slope in region I SCC). This second effect is highly nonlinear: it is insignificant for $Na_2O < 20\%$ but it becomes increasingly important above 20%, when sodium acts as a network modifier. Raman spectroscopy and Molecular Dynamics (MD) simulations aid in revealing the structural variations which arise from increasing concentrations of Na_2O. Na_2O causes the relative proportions of the different chemical bonds accessible in SBN glasses to vary. For this series of glasses, the Si–O–Si bond does not dominate the SCC properties. SCC variations originate in the mesoscale structure where sodium ions act as network modifiers on both the silica and borate units, thus yielding a partial depolymerization (i.e. a decrease in the reticulation level) of the network. This second effect reveals itself to be the one responsible for the SCC chemical dependency. Poisson's ratio increases approximately linearly with increasing Na_2O concentration, and thus, it is also not simply proportional to the slope in region I SCC. Partial depolymerization of the glass provides a novel prospective on the controlling factors in the sub-critical crack growth.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Stress-corrosion cracking is a phenomenon by which water (or other environmental factors) aids in the slow propagation of pre-cracks/flaws in materials. This slow propagation gains speed untimely leading to the overall failure of the material. This is one of the reasons why glass walkways (e.g. London Bridge, Grand Canyon, Yuntaishan Sky Walkway, Eiffel Tower…) have sacrificial protective glass panels which are removed when flaws are visible. In the absence of a corrosive environment, the stress intensity factor (i.e. stress felt by the crack front, K_I) must exceed the material's fracture toughness (K_c) for a crack front to propagate [1–3]. Yet, within a corrosive environment, water molecules attack the stretched network at the crack tip causing sub-critical crack propagation (i.e. $K_I < K_c$).

In general, three regions exist in the sub-critical cracking domain (Fig. 1). In region I, the crack front velocity, v, depends on the chemical reactions rates at the crack tip. In region II, the crack front velocity depends on the time for the water to reach the crack front. In region III, the crack front moves too fast for water to reach the crack front [1,4].

Occasionally, a fourth region, region 0 or the environmental limit (K_e), exists. K_e defines a threshold limit below which a crack front will not propagate.

Efforts to relate the SCC v as a function of K_I to the glass's chemical composition remain rather rudimentary as glasses are far too complex for a comprehensive analysis based on a rather small number of samples [1–5]. In these studies [1–5], a continuing hypotheses persists that the rupture of the Si–O–Si bond and/or the reaction rate theory control the SCC dynamics in region I [1–3]. This paper puts this hypothesis to test in SiO_2-Na_2O-B_2O_3 (SBN) glasses. Moreover, it will overturn this hypothesis for the SBN series and shows that the depolymerization (the amount of reticulation in the glass network) controls the sub-critical crack propagation.

This paper should be seen as the third in a series, the first two being Barlet et al. 2013 [6] and 2015 [7]. Ternary SBN glasses provide a simple model glass to examine the importance of a glass's chemical composition on its mechanical response in region 0 and I. Glasses herein contain two network formers (SiO_2 and B_2O_3) and one network modifier (Na_2O). These three components represent the major components for many industrial glasses; yet, little is known about how the chemical composition alters the stress corrosion cracking (SCC) properties. This paper examines v versus K_I curves for regions 0 and I for seven ternary

* Corresponding author.
E-mail address: cindy.rountree@cea.fr (C.L. Rountree).
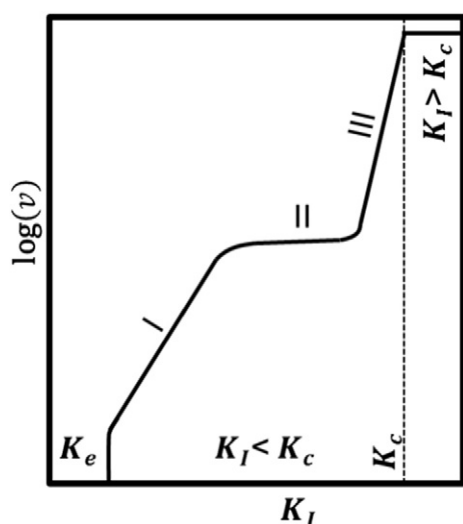
Fig. 1. Sketch of the 3 regions of sub-critical cracking commonly associated with stress corrosion cracking. In some materials, a region exists where the stresses at the crack tip are not sufficient for water to react with the crack tip, yielding an environmental limit, K_e [1].

SiO_2-Na_2O-B_2O_3 (SBN) glasses. Herein, K_e clearly shifts to higher environmental limits when Na_2O increases. On the other hand, SBN glasses display an increasing susceptibility to water as Na_2O increases [8] as evidenced by an increasing slope in region I. These results highlight Na_2O role on the mechanical behavior of glasses. Furthermore, they depend on Na_2O's role in the glass: network modifier or network charge compensator. Results herein reveal the depolymerization of the glass provides an indication of the stress corrosion cracking behavior in region I. These findings provide a new prospective on the controlling factors in sub-critical crack growth.

2. Methods

Barlet et al. 2013 [6] and 2015 [7] directly concern the series of SBN glasses presented herein and should be regarded as precursors to this paper. Most experimental and numerical protocols invoked in this study have been extensively tested and reported elsewhere. Thus, this section briefly reviews experimental and numerical protocols and references detailed works for further readings. The first Subsection 2.1 details the chemical composition of the 7 SBN glasses and recalls the standard way to characterize them. Subsection 2.2 describes fracture tests used to characterize the stress corrosion cracking (SCC) behavior. Subsection 2.3 details the spectroscopy tests used to analyze and characterize the structure of the glass. Subsection 2.4 recalls methods to acquire density, Poisson's ratio, and the Young's modulus. The last Subsection 2.5, details the numerical MD simulations which provide the structural organization of the atoms in the 7 SBN glasses.

2.1. Glass chemical composition

Glass fabrication invokes the same procedure as previously reported by the coauthors [6,7]. Table 3 recalls the target chemical composition of each glass [6]. A third party (PrimeVerre) verifies the glass chemical compositions via SEM-EDS (Environmental Scanning Electronic Microscope coupled with an Energy Dispersive Spectrometer) and/or ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy). SEM-EDS results revealed small amounts of impurities, <0.5%. Results reported herein are from ICP-AES measurements and have an uncertainty of 10%. Previous works by the co-authors examined and reported the chemical composition of the glasses along with their densities, glass structure, and hardness [6,7,9–11]. When possible, the same batch was used here as in the previous papers.

Table 1 recalls the measured ICP-AES, K_{SBN} ($\frac{[SiO_2]}{[B_2O_3]}$) where $[\cdot] \equiv$ mol% [6], R_{SBN} ($\frac{[Na_2O]}{[B_2O_3]}$), and density (ρ) presented in [6,7]. Sample classification herein concerns two K_{SBN} groupings: 2.52 ± 0.03 (blue series) and 4.6 ± 0.12 (red series). Grouping glasses via their K_{SBN} value provides a constant mol % ratio between $[SiO_2]$ and $[B_2O_3]$. A secondary parameter aids in categorizing the glasses: $R_{SBN} = \frac{[Na_2O]}{[B_2O_3]}$. Authors invoke the R_{SBN} and K_{SBN} parameters as they aid in estimating elementary units (BO_3 planar units, BO_4 tetrahedral, Metaborate units, pyroborate units, Silica tetrahedral with i ($i = 1$ to 4) bridging oxygen atoms) [6,12–14] and some macroscopic properties [7,13,15]. Thus, this notation will be continued herein.

2.2. SCC experimental set-up

SCC techniques invoke a well-documented procedure [16–20] which require DCDC (Double Cleavage Drilled Comparison) sample geometry ($5 \times 5 \times 25$ mm³ rectangular parallelepiped with a 1 mm diameter hole which passes through the 5×25 mm² faces). This geometry provides a decreasing K_I as the crack length grows [21,22]. Literature exemplifies stable crack propagation in region 0 and I for DCDC samples [23]. Pallares et al. [21] provides an updated version of He et al. [22] equation to calculate the stress intensity factor (K_I) at the crack tip based on the length of the crack (c):

$$K_I = \frac{\sigma \sqrt{\pi r}}{\left(a_o + a_1 \frac{w}{r} + a_2 \left(\frac{w}{r}\right)^2\right) + \left(a_3 + a_4 \frac{w}{r} + a_5 \left(\frac{w}{r}\right)^2\right) \frac{c}{r}} \quad (1)$$

where $\sigma = \frac{F}{A}$ is the stress applied to the sample, A is the surface area where the force F is applied, r is the radius of the cylindrical hole, w is the width of the specimen, and a_j ($j = 0$ to 5) are fitting parameters. Pallares et al. [21] calculated the following fitting parameters with Finite Element simulations for Eq. (1): $a_0 = 0.3156$, $a_1 = 0.7350$, $a_2 = 0.0346$, $a_3 = -0.4093$, $a_4 = 0.3794$, and $a_5 = -0.0257$.

A Deben compression machine applies the force on the 5×25 mm² facets. Initially, the applied force increases slowly until two precracks initiate off the hole. The cracks are then allowed to stabilize. Subsequently, the force is set and a tubular microscope coupled with Matlab programs images the crack front's displacement with the applied forces (see Fig. 2 for typical images) continuously. SCC runs occur with no direct control of the temperature nor humidity (i.e. ambient conditions). Researchers manually collected and logged temperature and humidity measurements. SCC experiments lasted from 1 week to 1 month. In order to limit temperature and humidity variations during a single SCC experiment, experiments are conducted in a chamber with limited contact with the external environment. The chamber was located in a room which rests underground and within the center of the building (i.e. none of the walls had direct contact with the outside). The average yearly temperature and humidity in the chamber was 30 ± 5°C and 40 ± 10%RH. Appendix A provides an indication of the average temperature and humidity during each experiment.

Post-image analysis provides the v versus K_I curves. When calculating the slope in region I, from time to time, outliers occur. These outliners are discarded in the slope calculations. Errors in slopes represent uncertainty obtained from fitting the points.

2.3. Structural characterization of the glass network

Barlet et al. [7] presents ^{11}B magic angle spinning (MAS) nuclear magnetic resonance (NMR) experimental methods and results for the SBN samples. Table 1 recalls the measured ^{11}B MAS NMR ratios of $^{[4]}B$ (amount of 4-coordinated boron), $^{[3]}B$ (amount of 3-coordinated boron) and presented in [6,7]. Post-analysis of ^{11}B MAS NMR gives