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Densification dependent yield criteria for sodium silicate glasses – An atomistic simulation approach

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ABSTRACT

Silicate glasses are macroscopically brittle but ductile at the micron scale. This plastic response is complex: in open structure materials, such as amorphous silica, plastic yield results in significant densification. While, more compact structures (e.g. soda-silicate glasses) are known to suppress densification and promote shear flow. We have carried out atomic scale simulations to analyze the plastic response of a series of silicates with increasing sodium content. Quasi-static, multi-axial deformation tests were performed on large samples ($\approx 10^3$ nm^3). Their yield behavior was quantified at different stress states, by measuring permanent volume changes. Qualitative agreement was found between the response of modeled systems and experimental results. Strong coupling between plastic yield and densification was observed. Our results also suggest that sodium silicates may densify not only under hydrostatic compression but also upon shear at large strains. Based on these numerical results, we propose a general yield criterion for soda-silicate glasses in which density is an internal variable. As density increases, the elliptic yield surface (characterizing amorphous silicates with open structures) gradually evolves into a Drucker-Prager-like model for fully densified samples.

1. Introduction

Silicate glasses are used for many technical purposes, especially where stiffness and transparency are required. Silicate glasses are brittle on the macroscopic scale but ductile at the micron scale [1]. This plastic response is expected to be key to understand brittleness. However, it was soon found that there is an unusual feature in the plastic response of amorphous silicates. Open structure glasses exhibit irreversible volumetric strain upon compression: for amorphous silica this densification saturates at ca. 20% at a hydrostatic pressure of about 20 GPa [2–5]. Moreover, for technical silicate glasses, sodium oxide (Na_2O) is usually added to silica, along with other compounds. Indeed, sodium modifies the silica network and lowers the glass transition temperature for easier glass processing. But the addition of sodium also impacts mechanical ductility. Upon hydrostatic compression soda-lime-silicates show less densification [6], and at reduced pressures values [7]. This behavior results from the phenomena that sodium gradually fills up the open structures.

In fact, the relation between densification and plastic yield in silicate glasses is a complex question, and a continuing matter of debate. Ever since densification was observed, the respective contribution of irreversible volumetric strain and shear flow has been an issue [8,9]. Experimentally, because larger samples break, nano-indentation was a useful tool. Unfortunately the resulting strain field of an indentation is very inhomogeneous, which helps little in the identification of a complex constitutive behavior. According to a rule of thumb, if pile-up is present – especially with very sharp indenters [10] – there is significant shear plasticity [11]. While if densification is dominant, the refractive index of the glass changes [12]. A large number of experiments was carried out, and the overall picture emerged: if densification is prevented, shear

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flow is enhanced. It was shown, that the addition of sodium [13,14] and pre-densification [15,16] decreases volumetric plasticity and increases shear flow.

However, for a more quantitative assessment of the competing processes, it is necessary to develop a continuum scale description of the governing plastic yield. Given the complexity of tests such as indentation, the use of advanced numerical tools and especially finite element modeling is inevitable. Compared to the large number of papers reporting indentation results, constitutive models for plastic yield in silicate glasses are few and far [17–20]. Moreover, these models must be calibrated using experimental results.

During indentation test force displacement curves are the usual indicators, however they are not very sensitive. To strengthen the experimental basis, a more elaborate identification of plasticity have been considered such as the measurement of residual stress (from crack patterns [21] or birefringence [22]) or density fields after indentation (from Raman scattering [23], luminescence [24] or chemical etching [25]). However, for a precise description other tests must be devised. The “simplest” one is probably the uniaxial compression test [26,27].

Once due consideration is given to these difficulties, it appears that numerical experiments may offer insight into the mechanical response of such complex materials. In this paper, our aim is to develop yield criteria from atomistic simulations for amorphous silicates, specifically considering the impact of composition. Given the present state of development of molecular dynamics, we do not expect these calculations to provide a quantitative characterization. Rather, we hope that our simulation results provide an explicit functional description of yield surface. Which model can then be made quantitative for given actual glass compositions, based on the various micron-scale mechanical experiments mentioned above, such as diamond anvil [28], pillar compression [26] or indentation tests [15].

In a pioneering work, Schuh and Lund [29] derived a constitutive relation from atomistic simulations for metallic glasses. Their numerically calculated yield surface compared favorably with experimental results. Since then, many works have been dedicated to measure plasticity in metallic glasses [29–33], nano-crystalline metals [34,35] and glassy polymers [36,37]. Amorphous solids in general were studied [38–40], though an elaborate quantitative description of silicate glasses is still missing. Simulations are very useful in this context, not only because they can provide detailed information about the mechanical response, but also because the underlying rearrangement mechanisms can be examined at the atom scale.

The paper is structured as follows. Section 2 introduces the numerical methods with details on molecular dynamics and statics [41]. In Section 3 results are given, first for simple hydrostatic compression and shear, then for the combined of the two. This is necessary to identify the constitutive behavior with strong coupling between volumetric and shear deformations. We show that the yield process can be rationalized when the evolution of density is considered. Finally in Section 4, a new form of yield function is proposed with the density as an internal variable.

2. Methods

Our aim is to simulate the mechanical response of amorphous silicate materials with open structures with increasing depolymerization.

2.1. Atomic sample preparation

The glass samples were generated by the random sequential placement of the atoms in a cubic simulation box with periodic boundary conditions. Molecular simulations were performed with LAMMPS [42] to equilibrate the liquid at 3000 K, to cool it using 10^{13} K/s quenching rate until ~0 K, and finally deform the samples. Atomic interactions were modeled with the empirical BKS potential [43] using the parameters of Yuan and Cormack [44]. The potential function was defined for the different pair interactions (e.g. Si–O, O–O or Na–O) with respect to the strong ionic/covalent Si–O bonds and the weaker but longer Na–O ones.[1]

To avoid the collapse of the atoms the short term potential was substituted with a repulsive function [45]. In this manner we have simulated three glasses xNa_2O-(100-x)SiO_2 with x = 5, 15, and 30% mol which will be referred to as NSx5, NSx15 and NSx30 following Yuan and Cormack [44]. The system sizes were 67 041, 69 849 and 73 368 atoms respectively with a final simulation box length of 10 nm. Thanks to this relatively large box, finite size effects are minimized. All samples were then compared with neutron [46], Brillouin [47] scattering and NMR [48–50] experiments to validate the initial structure. Agreement was found within the precision of the experimental results as shown also by Yuan and Cormack [44]. Further information about the sample generation can be found in Ref. [51].

2.2. Deformation scheme

To display a pressure dependent yield surface the main variables are pressure (p) and equivalent shear stress (k). Where $p = -\sigma_m$, and the average normal stress σ_m is calculated from the components of the diagonal of the Cauchy stress tensor ($\boldsymbol{\sigma}$): $\sigma_m = (\sigma_1+\sigma_2+\sigma_3)/3$, σ_i are the principal normal stresses.

Similarly, equivalent shear stress k can be expressed as: $k = J_2$, where J_2 is the second invariant of deviatoric stress tensor $\boldsymbol{s}$ ($\boldsymbol{s} = \boldsymbol{\sigma} - \sigma_m \boldsymbol{I}$, $\boldsymbol{I}$ is the identity matrix). J_2 can be given by the components of the Cauchy stress tensor ($\boldsymbol{\sigma}$) as well:

$$J_2 = \frac{1}{6}\left((\sigma_1-\sigma_2)^2 + (\sigma_1-\sigma_3)^2 + (\sigma_2-\sigma_3)^2\right). \quad (1)$$

In addition, we have also studied the impact of the third stress invariant $J_3 = \det(\boldsymbol{s})$. Therefore, we will also use the Haigh-Westergaard (HW) stress space [52–58], where the three independent variables are:

- hydrostatic stress $\rho = -p\sqrt{3}$,
- deviatoric stress $s = k\sqrt{2} = \sqrt{2J_2}$,
- meridian angle (or Lode angle) - ϑ.

The meridian angle (ϑ) is defined as [59]:

$$\cos 3\vartheta = \frac{3\sqrt{3}}{2}\frac{J_3}{J_2^{3/2}}. \quad (2)$$

Note the opposite sign convention for pressure and hydrostatic stress: in compression pressure is positive while hydrostatic stress is negative. The third variable (ϑ) in the HW stress space indicates whether the deviatoric stress tensor is predominantly tensile ($\vartheta = 0°$), shear ($\vartheta = 30°$) or compressive ($\vartheta = 60°$).

The deformation was applied in a quasi-static way [41]. During both compression and tension the dimensions of the simulation box was reduced by a constant displacement step, while the positions of the particles were rescaled in a homogeneous way. After box

[1] The cutoff values used for the potential function were fine-tuned in order to achieve the experimentally measured densities (2.238, 2.340 and 2.470 g/cm^3) at ambient pressure. Therefore, we used a parameter r_{cut} equal to 5.1, 5.9, 6.9 Å for NSx5, NSx15 and NSx30 samples respectively.