Acta Materialia 114 (2016) 146–153

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

Perfectly plastic flow in silica glass

G. Kermouche [a, *], G. Guillonneau [b], J. Michler [b], J. Teisseire [c], E. Barthel [d]

[a] University of Lyon, Ecole des Mines de Saint-Etienne, SMS Division, LGF UMR5307 CNRS, 42023 Saint-Etienne Cedex 2, France
[b] Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Mechanics of Materials and Nanostructures, Thun, Switzerland
[c] Surface du Verre et Interfaces, CNRS/Saint-Gobain, UMR 125, 93303 Aubervilliers Cedex, France
[d] ESPCI ParisTech CNRS UPMC, Soft Matter Science and Engineering, Paris, France

ARTICLE INFO

Article history:
Received 9 October 2015
Received in revised form
25 February 2016
Accepted 13 May 2016

Keywords:
Amorphous silica
Micropillars
Densification
Shear flow
Fracture
In situ testing
Finite element analysis

ABSTRACT

The plastic behavior of silicate glasses has emerged as a central concept for the understanding of glass strength. Here we address the issue of shear-hardening in amorphous silica. Using *in situ* SEM mechanical testing with a high stiffness device, we have been able to compress silica pillars to large strains while directly monitoring radial strain. The sizeable increase of pillar cross-section during compression directly demonstrates the significant role of homogeneous shear flow. From the direct evaluation of the cross section, we have also measured true stress-strain curves. The results demonstrate that silica predominantly experiences plastic shear flow but that there is no shear-induced hardening. The consequence of this finding for our understanding of glass strength is discussed.

1. Introduction

Strength is an issue as old as silicate glasses. Even after thousands of years, novel compositions for stronger glasses are still actively being sought [1,2] as a clear understanding of intrinsic glass strength is still missing. Ordinary levels (tens of MPa) of glass brittleness result from large surface defects that enable crack initiation and subsequent propagation, while carefully prepared samples exhibit intrinsic strengths of several GPa [3]. Simultaneously, it is now well-known that below a given lengthscale, of the order of micrometers, silicate glasses undergo plastic deformation [4–6]. An intriguing question is the connection between plastic strain and the formation of crack-initiating defects [3,7,8]. Another puzzling issue is the discrepancy between surface energy [9] and fracture energy [10], which for silicate glasses differ by one order of magnitude. Finally, recent observations show that the elastic singular field near the crack tip extends to about 10 nm from the crack tip. These results suggest a contribution of plasticity near the fracture tip. To better assess this contribution, a better understanding of plasticity in silicate glasses is required.

In the standard model of plasticity, plastic deformation conserves volume and plastic deformation proceeds by homogeneous shear flow. This picture applies to many polycrystalline metals, semiconductors, and ceramics. The plastic deformation mechanisms in amorphous materials like silicate glasses are rather different from the dislocation-based plastic flow of crystalline materials. One difficulty with glassy materials is that shear flow often induces localization of shear. A very strong shear strain appears in very thin shear bands, while there is virtually no shear in the blocks delimited by the bands. Besides this strong heterogeneity, another difficulty comes from the role of densification. Silicate glasses with a very open structure can exhibit a significant irreversible volumetric strain in addition to the more standard shear flow. Vitreous silica, for instance, can reach up to 20% permanent densification above a hydrostatic pressure of 20 GPa [11–13].

Ever since densification has been identified, a major issue has been the respective contributions of plastic shear flow and densification in indentation [14]. Peter [15] demonstrated significant pile-up in soda-lime glass, which was interpreted as clear evidence of shear flow mediated by shear bands. In fact, he used a very sharp tip to enhance the formation of pile-up. Arguments for densification often rely upon Mackenzie's observation that densification in

* Corresponding author.
E-mail address: kermouche@emse.fr (G. Kermouche).

http://dx.doi.org/10.1016/j.actamat.2016.05.027
1359-6454/

silica is at least partly reversible, even at temperatures significantly below the glass transition [16]. As a result, elaborate experiments have been carried out to evaluate the respective contributions of densification and shear flow by monitoring the relaxation of the compaction. These experiments are mostly based on the analysis of indent shape (indented volume and pile up size), both before and after relaxation at temperatures close to Tg.

As a result of numerous experiments, the accepted picture is that densification is largely dominant in anomalous glasses such as vitreous silica [1]as in recent compression tests carried out on micro-sized silica balls which suggest that plasticity can be fully accommodated by densification [17]. Shear flow, on the other hand, rules the plastic deformation of soda-lime glasses [18], and is usually present in the form of shear bands. Normal glasses predominantly exhibit shear flow [12,19,20]. A transition from anomalous to normal is thought to take place as free volume decreases, as recently evidenced by extensive experimental investigation on soda-lime glasses [21] and a wide-range comparison of various glasses [22]. In this latter study, pile-up is absent in pristine fused silica, but emerges if silica is pre-densified.

Beyond qualitative evaluation, attempts have been made to provide a more quantitative description of the plastic response of silicate glasses. With such a constitutive equation, mechanical response for all types of loadings can be calculated. In indentation experiments [22–24], the stress state is a complex spatial distribution of combinations of high hydrostatic pressure and shear present in roughly equal proportions [25,26]. It appears that indentation experiments can be reproduced using either yield rules coupling shear flow and densification [24,27,28], or a yield rule that only accounts for densification [29]. More data is needed beyond the indentation force-displacement curves to conclude which rule is more applicable. Many investigations dealing with silica microplasticity have been carried out with high hydrostatic pressure experiments [30,13]; they are very useful, but lack the necessary shear contribution. It has also been proposed to use the indentation-induced densification field, which can be measured by Raman scattering [23,31], or by silica dissolution experiments [32], but there are discrepancies between these data.

Recently quasi-uniaxial compression experiments of silica disks have been carried out inside a diamond anvil cell [35]. The axial compression was applied by direct contact with the diamond flats. It was found that this quasi-uniaxial compression induces a large radial expansion, which can only be explained by a dominant shear flow. In fact the authors demonstrated that silica can deform up to very large uniaxial strain (close to 1.0). They concluded that the level of plastic shear-based deformation can be very high for silica, even at room temperature. These results confirmed our micro-pillar compression tests where we demonstrated stable plastic flow up to 20% by post-mortem SEM pillar observations with significant contribution of radial flow during straining [26]. These quasi-uniaxial compression experiments differ from indentation in that the ratio of hydrostatic pressure to shear stress is much lower in the absence of radial confinement.

Interestingly Wakabayashi et al. [35] also reported a significant level of strain hardening. Indeed, hardening is also an important issue. First, hardening is intrinsically related to the way the plastic flow modifies the material, and as a result impacts its mechanical response. In crystalline materials, shear-hardening is a consequence of dislocation interactions [36], with strong impact on the macroscopic response. For instance, hardening is known to prevent pile-up formation in indentation experiments [37] on standard metallic systems. In contrast, strain softening is known to generate the instability which results in shear bands. In fact, shear hardening has never been explicitly addressed in silicate glasses, although it would affect the residual stress field [40], damage evolution, and crack propagation [41]. Therefore the claim that there is shear hardening in the plastic deformation of amorphous silica is remarkable as it would: 1) pave the way to strong glasses 2) challenge our understanding of the plastic deformation mechanisms of silicate glasses.

In fact we have previously introduced some form of hardening in the constitutive relation for silica, but this specific form of hardening was coupled only to the densification process [11,24] and not to shear flow. In an atomistic picture, this hardening is mainly driven by the reduction of free volume [38,39], as observed in porous materials. A simple state variable such as porosity was defined to account for this form of hardening [31]. Implicitly, however, we assumed in this constitutive relation that there is no hardening for plastic shear flow.

In this paper, we address issues of shear flow and shear-hardening of amorphous silica. For that purpose, we have performed uniaxial compression of silica pillars in an *in situ* SEM compression set-up with high stiffness. With this device we can drive the material into a state of large uniaxial plastic deformation while monitoring the cross section for an accurate true stress-strain curves. The results are analyzed in terms of competition between densification and plastic shear flow. They demonstrate that in uniaxial compression silica predominantly experiences shear flow and that there is no shear hardening.

2. Materials and methods

2.1. Pillars fabrication and geometry

The pillars were fabricated on amorphous silica wafers (3 inches, one-side polished, 1 mm thick, GE124, Won Ik Quartz Europe GmbH) by deposition of an electroplated Ni mask (REF [B]) followed by plasma-based reactive ion etching (RIE) (REF A). The C4F8/He mixture exploits both chemical and physical processes to remove solid material locally. The residual nickel layer is removed using Nichrome Etchant TFN (Transene Company). Compared to the focused ion beam (FIB) process commonly used for metal pillars, RIE allows for large series of micrometric pillars to be fabricated over areas of the order of one centimeter in a single run.

The final dimensions of the pillars were measured by scanning electron microscopy (SEM-FEG, Fig. 1). Pillars have a truncated cone shape characterized by a semi-angle of 96±0.5, an upper diameter of 4.8±0.1 μm, and a height of about 4 ± 0.005 μm. Overall the

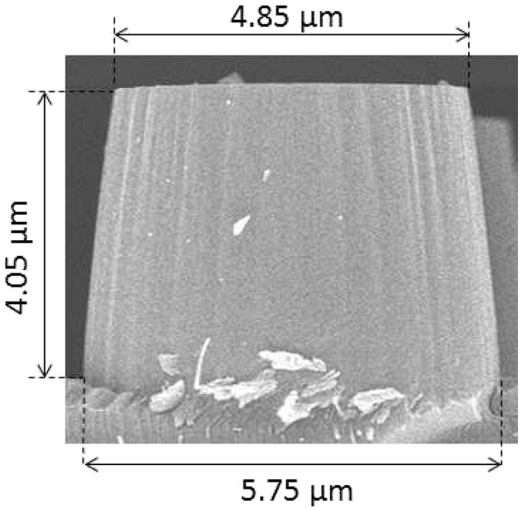

Fig. 1. Micro-pillar geometry before compression.