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A 2000-year perspective on indentation crack resistance and brittleness of glass

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ABSTRACT

Data on micromechanical properties of ancient and medieval glass fragments and glasses of early modern and today's manufacturing were compiled to offer a tentative look on changes in the brittleness of glass over the past 2000 years. Chronology of glass making was based on glass chemistry using rare earth element (REE) pattern, fluxing agents and provenance analysis while cracking and brittleness were evaluated from Vickers indentation in the course of the mean crack initiation load *CR* and the crack length-to-half diagonal ratio *c*/*a*. A structural analysis revealed that *CR* increases and *c*/*a* decreases with increasing molar volume i.e. decreasing atomic packing fraction, which allows us to classify periods of high and low crack-resistant and brittle glasses along the time line of historic glass technology.

1. Introduction

Due to their brittle character glasses exhibit a poor and uneven resistance to fatigue that makes their reliability questionable. Thus, overcoming the brittleness of glass is a key challenge for the development of high performance materials in the 21st Century [1,2]. Beside classical implementation of compressive stresses into the glass surface through thermal quenching and sub-T_g ion exchange, a new pathway to toughening glasses was recently proposed such as topologically engineered glass structures [3], crack self-healing capacity [4] and the design of a 3D micro-crack architecture in the glass sub-surface [5]. On the other hand glass technology has been a subject of continuous development over the past 2000 years driven by the accessibility of resources (raw materials) such as fluxes and useful sand qualities, by changing melting (from pot to tank) and forming processes (pre-industrial manufacturing vs. modern glasses of high workability) as well as by today's integration of ecological requirements in the economic demands of a global glass market.

In view of the above and considering the current understanding in structural design for less brittle silicate glasses such as controlling ring size distribution, number of non-bridging oxygens and mobility of network modifier ions [2] on one hand and atomic packing factor and Poisson's ratio [6] on the other hand, it is may be helpful to take a look back at some of the milestones in the history of glass manufacturing. The paper aims therefore to offer a tentative look on changes in the brittleness of glass over the past 2000 years.

In this article we provide for the first time data on mechanical properties of ancient and medieval glass fragments and glasses of early modern and today's manufacturing in a chronological order by considering their geochemical fingerprints, which corresponds to different epochs of glass technology. In particular dating of glass fragments was based beside provenance on glass chemistry using rare earth element (REE) pattern and flux composition. The former is capable to classify archeological glasses in the three major types soda-lime, soda-ash and wood-ash by relating their chemical composition to the continuous upper rock layer of the continental crust (CC). In particular the concentration of rare earth elements (REE) La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu in the glasses normalized to the abundance in the earth's continental crust were used [7,8]. On the other side micromechanical properties of archeological glass fragments were investigated. In particular indentation experiments on cross sections of the glass fragments were performed to avoid perturbations from altered surface structures [9] and to obtain hardness, brittleness and crack resistance data from the bulk of the fragments.

2. Experimental

2.1. Samples description and preparation

Glass fragments H1, H2, R1, R2, R3, R4 and M1, M2 were provided with the kind assent of Prof. Dr. Sait Başaran, Director of Excavations

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by his researcher team of the archeological site of Enez (ancient city of Ainos)-Turkey, while medieval glass fragments were obtained from excavations at Brunshausen, Germany (Bru15, Bru16, Bru19) [10] and Mainz, Germany (Mz9) [11]. A glass fragment (N1) of early Modern manufacturing was excavated at a construction site in Clausthal, Germany. The survey of historic glasses was supplemented with data of a commercial soda-lime float-glass (G1) (S. Cramm, unpublished data) and two ternary soda-lime-silica model glasses (G2 [12] and G3 [13]) of similar composition as well as an alkaline earth aluminoborosilicate display glass (J1) [14] and Asahi "less-brittle" glass (S1) of composition $13Na_2O$, $1K_2O$, 4MgO, 1CaO, $2Al_2O_3$ $79SiO_2$ [15] to reflect the spread in brittleness of today's manufacturing.

Small parts (ca. 2 mm^2) were cut from the individual glass fragments and mounted in epoxy resin blocks perpendicular to the original glass surface. Subsequently the surfaces of the cross-sections were ground and polished with a 1 μm diamond paste.

2.2. Laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS)

The chemical composition of the glasses was determined by continuous ablation of material from the glass surface with a 10 Hz pulsed ArF-Excimer Laser (Compex 110, Lambda Physik, Göttingen, Germany) with 193 nm wavelength and about 5 J cm^{-2} energy (spotsize 120 μm, depth about 500 μm). The ablated material is transported via an Ar-flow into the inductively coupled plasma (ICP) ion source of a quadrupole mass spectrometer (Perkin Elmer Elan DRC II, Canada). About 70 isotopes were counted for 10 ms each resulting in a complete mass spectrum in about a second time. About 200 spectra are recorded to aim good statistics. The measured intensities were transformed into concentrations by applying an external calibration with NBS610 (NIST, USA) reference material, an internal standardization with ^{29}Si as internal standard element, and by summing up all major elements to 100%.

2.3. Vickers indentation

Two series of Vickers indentation experiments were carried out to determine basic micro-mechanical properties. In the first series indentation was performed at a load of 9.81 N for a dwell time of 15 s with a micro indenter (Shimadzu HV2000, Kyoto, Japan). Subsequently 3D laser scanning microscopy (Keyence VK-9700, Keyence, Osaka, Japan) was used to measure the crack length of each indent directly after the indentation (time delay between indentation and microscopy is in the range of 20 s). The confocal system of the microscope is equipped with one white light source and one laser source ($\lambda = 408$ nm), which allows to obtain high-resolution images both perpendicular to optic axis (spatial resolution ≈ 200 nm) and along the optic axis (height resolution ≈ 1 nm). From the average of the two diagonals of each indent the hardness (H_V) was then calculated as

$$H_V = \frac{P}{\alpha_0 a^2} \quad (1)$$

where P is the load (N), α_0 is the indenter geometry constant (2.157×10^{-3} for Vickers) and a is the half diagonal of the indent (μm). From the ratio of the length of the radial corner cracks c and indent half-diagonal a the brittleness B was calculated according to Seghal et al. [16]:

$$B = f \frac{1}{P^{1/4}} \left(\frac{c}{a}\right)^{3/2} \quad (2)$$

with the numerical factor $f = 2.39\ N^{0.25}\ \mu m^{-0.5}$.

We note that Vickers indentation is a non-recommended technique for analyzing brittle failure and thus fracture toughness of glasses. Quinn and Bradt [17] have clearly demonstrated that in R-curve-dependent polycrystalline ceramics, the fracture toughness determined using the parameters obtained from Vickers indentation (K_I) does not correspond to the fracture toughness obtained using standardized tests. K_I corresponds to a single point on the R-curve, which is different from that of the standard tests (K_{IC}) and K_I values should therefore only be used for internal comparison. For homogeneous glasses, however, extrinsic and intrinsic microstructural toughening behind and ahead of the crack tip is absent [18]. Thus, Vullo and Davis [19] have shown that the results obtained for glasses using the indentation method are strongly correlated with fracture toughness values measured using standard techniques, such as Chevron notch, where a defined defect is applied to the glass surface before under 3-point bending the crack propagates until failure is observed. However, due to the insufficient volume and geometry of the ancient glass fragments standard tests were not applicable. Hence in this study, we have evaluated the brittle character of the glasses by the crack length-to-indent size ratio from Vickers indentation tests. Further in the second series of indentations the probability to generate a radial crack was taken as a measure of brittleness. In this series indents at lower loads (0.3–1.5 N, 10 indents per load) were performed with a sub-micro indenter (UNAT-M, Asmec, Radeberg, Germany) to determine the crack resistance CR for the load initiating in average two of four of radial cracks at the corner of the indents according to the method of Wada et al. [20].

We note further, that mounting the glass fragments of different thickness may cause secondary effects in terms of the convolution of polymer and glass mechanics. Finally, we are fully aware that polishing the samples (diamond, 1 μm) causes alterations of the near surface region, which has not been the focus of the present study.

3. Results

3.1. Chemistry and dating of glass fragments

Fig. 1 shows the normalized REE-concentrations of the studied glass fragments as classified to characteristic pattern of wood-ash, soda-lime and soda-ash glasses [7]. Fragments Bru15, Bru16, Bru19, Mz9 and also N1 were assigned to wood ash glasses since a strong negative Eu-anomaly is observable, which is a typical signal for granites from the normal continental crust as source for the quartz used in wood-ash glasses [22,23]. In contrast to all the used fluxes the REE-concentration in beech ash (data from [7]) is as high as in sandstones and exhibits almost the same continental signature. On the other side soda ash M1, R1, R3 and R4 and soda lime glasses H1, H2, M2, R2 showed a slight increase in the heavy REE-concentration (HREE), which is explained by the use of quartz coming from residual (depleted) earth's continental crust due to partial melting and production of granitic melts, in which the light REE-concentration (LREE) is enhanced [7]. The accumulation of the HREE is somewhat higher in the soda-lime glasses compared to the soda-ash type. The used flux for production of soda-ash glass (ashes from halophytic plants) plays no role, because their REE-concentrations are remarkably lower (ca. $\approx 10^{-7}$) than in the quartz derived from sandstones. Also the REE-concentration in trona about 10^{-3}–10^{-4} is not sufficient enough to affect the REE-pattern of the soda-lime glasses (see [24,7]).

The above classification is supported by analyzing the fluxing agent concentrations with respect to the ternary mass fractions w_{Na2O}, $w_{(K2O\ +\ MgO)}$ and w_{CaO} (Fig. 2). According to Gratuze & Janssens [25] the fragments H1, H2, R2 and M2 are members of the natron soda-lime glass group (1), the fragments R1, R3, R4 and M1 belong to the plant ashes soda-lime glasses (2), while fragments N1, Bru15, Bru16, Bru19 and Mz9 are forest plant ashes potash-lime glasses (4).

In order to achieve a provisional chronology of the soda-lime and soda-ash glasses from the ancient city of Ainos we compared their K_2O-to-MgO ratios with those of the early (4th–7th century CE), middle (8th–9th century CE) and late (12th–14th century CE) Byzantinic period glasses excavated in Bergama (ancient city of Pergamon, Asia Minor)