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Subcritical crack growth and power law exponent of Y–Si–Al–O (–N) glasses in aqueous environment

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Abstract The subcritical crack growth resistance in water of a Y–Si–Al–O and Y–Si–Al–O–N glasses has been investigated with three point bending experiments. It has been shown that the SCG behaviour of the Y–Si–Al–O–N glass is superior to that of the Y–Si–Al–O glass. This is reflected by the power law exponent *n* which is 21 for the Y–Si–Al–O glass and 63 for the Y–Si–Al–O–N glass. Mechanistic implications of these observations are discussed.

Introduction

Y–Si–Al–O–N glasses are renowned for their extremely high mechanical durability [1]. It has long been shown that the incorporation of nitrogen strengthens the internal glass network. Lately it has also become clear that Y–Si–Al–O–N glasses possess a very high resistance against water induced subcritical crack growth (SCG) [2, 3]. This would make these glasses, a sensible alternative for applications where the glasses have to sustain mechanical loading under humid conditions; for instance of joining applications [4], fibres [5] or scratch resistant coatings and glasses [1].

However the extend to which the incorporated nitrogen is responsible for the improved SCG resistance may be questioned, since little to none is known about the SCG resistance of rare earth aluminosilicate glasses themselves. It is therefore the aim of this investigation to determine whether the high SCG resistance of Y–Si–Al–O–N glasses can be attributed to the incorporation of nitrogen or if it simply is a base property of the Y–Si–Al–O glass matrix.

For that goal, a Y–Si–Al–O–N glass has been prepared as well as a corresponding Y–Si–Al–O glass. Their slow crack growth resistance has been compared. In order to validate the method used, a commercial borosilicate glass has been included in this investigation.

Experimental

The two compositions of the glasses prepared in this investigation are $Y_{11.5}Si_{14}Al_{11.5}O_{63}$ and $Y_{15.2}Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ (at%). A difference in the (cationic) composition is unavoidable due to the shape of the glass-forming region. However this is not expected to have a large impact on the slow crack growth behaviour. For both compositions, data on the mechanical properties are already available from other authors [6, 7]. The Y–Si–Al–O(–N) glasses were prepared from Y_2O_3 (Shin Etsu), SiO_2 (amorphous, 99.7%, CE-minerals), Al_2O_3 (Taimei 4N) and Si_3N_4 (Akzo Nobel P95H). Batches of 50 g powder were mixed by ball milling (isopropanol, Si_3N_4 balls), dried and placed in a graphite crucible with BN powder lining to prevent sticking. The glasses were melted for 1 h at temperatures of 1600 °C (Y–Si–Al–O) and 1700 °C (Y–Si–Al–O–N) in an electrical furnace under a nitrogen atmosphere. The glasses were rapidly cooled by retracting the crucibles from the furnace. They were

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then placed in an annealing furnace operating at 800 °C (Y–Si–Al–O) and 900 °C (Y–Si–Al–O–N) in air, after which they were cooled down slowly to room temperature. The surface of glass ingots was ground down to dispose of an oxide scale, which had formed during the cooling process. The borosilicate glass was used as received.

The density of the glasses was determined (Archimedes principle) and the Young's modulus was measured (Ultrasonic pulse-echo measurements). The hardness was determined as a function of the load (P = 100, 200, 300, 500, 1000, 2000 g). The measured indentation diagonals (d_{m}), which are load dependent, were converted to a load independent hardness (H_{v}^{0}) and an elastic recovery parameter (δ) in order to compensate for the indentation size effect according to the relation [8, 9].

$$H_{\mathrm{v}} = H_{\mathrm{v}}^{0}\left(1 + \frac{\delta}{d_{\mathrm{m}}}\right)^{2}. \tag{1}$$

The Y–Si–Al–O(–N) glass ingots were then further diamond cut to bending bars with a height and width of 2 and 3 mm, respectively, and a length of 14 mm. The borosilicate glass was cut into specimens with a dimension of 2 × 4 × 20 mm. A Vickers indent was made on the tensile surface of the specimen in order to provide an initiation point for the crack and to limit the experimental scatter in the failure stress data. For the Y–Si–Al–O(–N) glasses an indentation load of 1,000 g was used. For the borosilicate Schott/Duran glass this was 500 g. The bars were tested immediately after indentation in deionised water in a three point bending configuration (10 mm span) in which the stress rate ($\dot{\sigma}$) was varied. After breaking, the bar was examined with an optical microscope to determine whether the crack initiated from the indent. If this was not the case the datapoint was rejected.

Two experimental set-ups were used to determine the failure stress. Higher stress rates were achieved with a conventional testing machine (TesT). These experiments were executed at a constant crosshead velocity and from the logged data the stress rate was determined. For low stress rates another set-up was used in which the weight of a water-filled container is transferred via a lever construction to the sample. By slowly filling the container with water a constant increase of the loading force can be achieved. Afterwards, the results of both tests were combined to yield the full failure curve. The relation between the failure stress (σ_{f}) to the stress rate ($\dot{\sigma}$) for indented specimens is given by [10]

$$\sigma_{\mathrm{f}} = A'(n' + 1)\dot{\sigma}^{\frac{1}{n'+1}} \tag{2}$$

with A' a constant related to v_0. The SCG parameter n' was determined by plotting the stress rate versus the failure stress on a double logarithmic scale and determining the slope by linear regression. The n' value for indented specimens can be translated to the standard power law exponent (n) by

$$n' = \frac{3}{4}n + \frac{1}{2} \tag{3}$$

which relates to the crack velocity (V) according to the familiar power law:

$$V = A\left(\frac{K_{\mathrm{I}}}{K_{\mathrm{Ic}}}\right)^{n}. \tag{4}$$

Results

Both the Y–Si–Al–O and the Y–Si–Al–O–N glass were completely transparent though greyish in appearance, which is common for these materials. Figure 1 shows the raw data for the hardness measurements, while Table 1 gives an overview of the measured properties for the three glasses. From the data it becomes immediately apparent that the mechanical performance improves going from the borosilicate to the oxide to the oxynitride glass. In the case of the Y–Si–Al–O glass one would expect the glass network to be further developed than in the case of the borosilicate glass. The reason for this lies in the addition of both aluminium and yttrium.

Although Y^{3+} acts as a network modifier, its effect on the glass network is limited due to its relatively small size and low coordination number [11]. There are

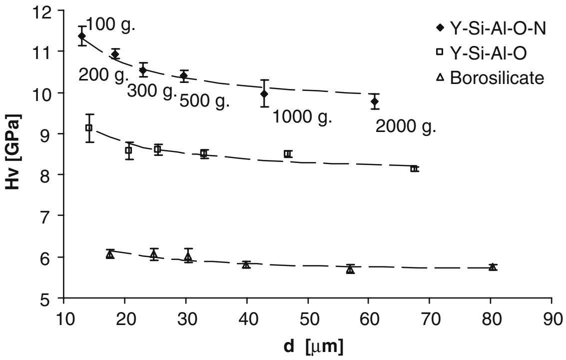

Fig. 1 Measured hardness as a function of the indentation diagonal

Table 1 Density (ρ), Young's modulus (E), intrinsic hardness (H_v^0), elastic recovery parameter (δ), number of bend specimens and n-value (with a 90% confidence interval) for the glasses studied in this investigation. The density and the Young's modulus are compared with literature data

	ρ (g/cm^3)	E (GPa)	H_v^0 (GPa)	δ (μm)	No spec	n (90% conf)
Schott Duran ®	2.505	60	5.6	0.8	63	15 (13–19)
Y–Si–Al–O	3.588 (3.572 [6])	110 (112 [6])	8.0	1.0	72	21 (16–29)
Y–Si–Al–O–N	3.985 (3.97 [7])	145 (146 [7])	9.6	1.1	72	63 (33–404)

even some indications that Y^{3+} can substitute for Si^{4+} on a tetrahedral site and thus can act as a network former rather than a modifier [12].

These factors contribute to a very strong, interlinked glass network and therefore explain the very strong mechanical performance of Y–Si–Al–O glasses as has been observed for e.g. the hardness and the Young's modulus. When Si_3N_4 is added to this system the rigidity of the network is further increased by the ability of nitrogen to form three covalent bonds with silicon instead of oxygen, which binds only two at maximum. The Si–N binding is not stronger than that of Si–O, but the higher coordination leads to a somewhat higher bond density in the glass, which improves the mechanical durability. A further effect is expected from the very high resistance against bending of the NSi_3 unit as compared with the OSi_2 unit [13]. These factors seem to be consistent with the observed improvement of the mechanical properties. However some care must be taken when directly comparing these values because of the different contents of yttrium and aluminium between the oxynitride and the oxide glass.

The determined power law exponents (n) show a large difference between the oxide and oxynitride glasses. The value of $n = 15$ ($n' = 12$), obtained for the borosilicate glass (Fig. 2) corresponds exactly to the findings of Fett et al. [14], thus showing the viability of the method used. This is a normal value for silicate-based glasses: e.g. soda-lime gives a value of $n = 17.9$ [10]. The value for the Y–Si–Al–O glass is already quite high $n = 21$ ($n' = 16$) (Table 1, Fig. 3), this possibly is a result of the high degree of cross-linkage in these glasses. However, the power law exponent for the Y–Si–Al–O–N glass is significantly higher than that of conventional silicate glasses ($n = 63$) ($n' = 47$, Fig. 3), it even approaches that of Si_3N_4 itself. As with the results of Coon ($n = 142$, [2]) and Bhatnagar et al. ($n = 46$, [3]) for oxynitride glasses, these results are markedly higher than for oxide glasses. Therefore it is clear that the introduction of nitrogen leads to a strongly improved slow crack growth resistance.

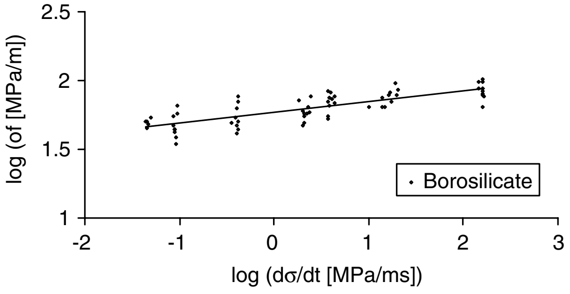

Fig. 2 Failure stress versus stress rate for the Duran glass

This presents an interesting dilemma. How can the addition of a relatively small amount of Si_3N_4 have such a dramatic effect on the SCG resistance? There is no satisfactory explanation, how nitrogen, which only performs approximately 10–15% of the overall bonding can be responsible for this increase. Current explanations are focussed on the creation of areas of high resistance against environmentally assisted rupture by nitrogen. While this may be true to some extend, one can also think of ways by which nitrogen can eliminate weak spots in the glass structure, since this would have an even stronger effect on the SCG resistance.

It has been suggested that such a critical step in the SCG of vitreous silica is the straining and subsequent the hydrolysis of 3-fold –O–Si-ring structures in the glass (Fig. 4, [15, 16]). In an inert environment these rings provide a substantial contribution to the fracture energy. However in the presence of water they are surprisingly easy to break.

The same has been assumed for –Te–O-rings in tellurite glasses. But in tellurite glasses these ring

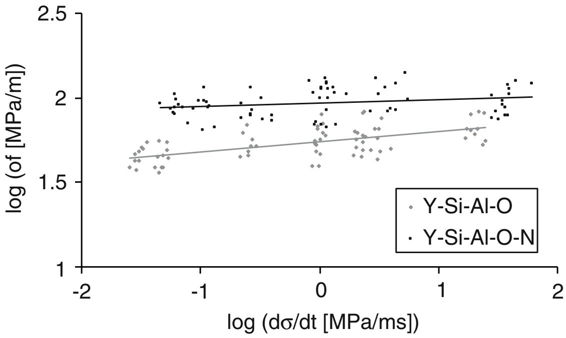

Fig. 3 Failure stress versus stress rate for the Y–Si–Al–O and Y–Si–Al–O–N glass

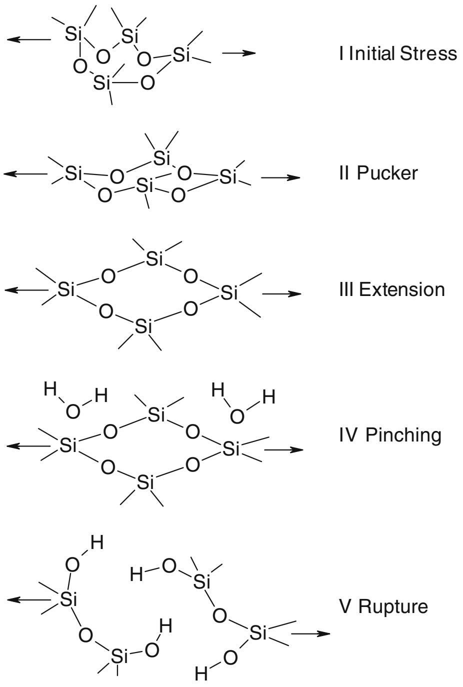

Fig. 4 The five stages of ring deformation and water-assisted rupture according to Michalske and Bunker [16]

structures are shown to be absent which attributes to the high SCG resistance. Power law exponents ranging from 50 to 70 have been reported for these glasses [17].

In oxynitride glasses the incorporation of nitrogen in silicate rings will most likely impede the formation of reactive sites due to the bending constraints of the Si–N–Si bond. However, in Y–Si–Al–O–N glasses there is also evidence for the suppression of these ring structures. The composition, which is used here, crystallises in the form of the "B-phase" (Y_2SiAlO_5N). This phase has the pseudo α-wollastonite structure. Whereas one would expect this structure to consist of layers of yttrium cations and rings of three corner-sharing $(Si,Al)(O,N)_4$ tetrahedra. It is shown in recent work that the formation of these rings is suppressed by the incorporated nitrogen [18]. Since glasses are known to share many structural characteristics with their low temperature crystalline phases, three-membered rings are likely to be absent in the glass as well, which would lead to a plausible explanation for their high SCG resistance.

Conclusions

This investigation has shown, that Y–Si–Al–O glasses display a good resistance against SCG in a water environment. However, the SCG resistance of Y–Si–Al–O–N glass is by far superior to that of Y–Si–Al–O indicating that the incorporated nitrogen is indeed responsible for the very high SCG resistance observed in previous investigations. It is argued that the incorporated nitrogen intervenes in one of the critical steps of the slow crack growth mechanism.

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