The Role of Water in the Mechanical Fatigue of Glasses

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ABSTRACT

Crack initiation plays an important role in the mechanical fatigue of many glasses. It was shown earlier that only water (and ammonia) can cause crack initiation under sub-critical stress by entering a glass due to stress-accelerated diffusion. The mechanical properties of glasses containing water were investigated to clarify the process of crack initiation. It was found that the critical stress at which permanent deformation takes place decreases with water content and with stressing time. This can cause the reduction of the crack initiation stress and can explain the fracture strength degradation with time for water-containing glasses in paraffin oil and many conventional oxide glasses in a water vapor-containing atmosphere.

KEYWORDS

Glass; fatigue; water; microhardness; crack initiation.

INTRODUCTION

It is well recognized (Proctor et al., 1966) that water causes mechanical fatigue of glasses. Water also promotes slow crack growth in glassees (Wiederhorn, 1967) and it is usually assumed that mechanical fatigue and slow crack growth are related (Evans, 1974; Evans and Wiederhorn, 1974). Namely, the mechanical fatigue is often explained in terms of slow crack growth. This explanation is valid only if a glass specimen which exhibits mechanical fatigue has the same crack tip geometry as a slowly propagating crack. If the specimen has a different crack tip geometry from the propagating crack, for example, if the specimen initially had a blunt crack tip (or notch), its fatigue lifetime cannot be equal to the time for slow crack growth since it involves the time for initiating a sharp crack.

In our earlier investigations (Ito and Tomozawa, 1982a; Bando et al., 1982; Hirao and Tomozawa, 1987a, b), it was shown that the crack tip of glasses can be made blunt either by annealing in air or by a hot water treatment, and that these treated glasses with blunt crack tips showed a different mechanical fatigue behavior from freshly abraded glasses with sharp crack tips. It was found (Hirao and Tomozawa, 1987b) that while the fatigue behavior of freshly abraded glasses with sharp crack tips can be explained in terms of slow crack growth, those of the glasses with blunt crack tips cannot since the fatigue lifetime for these consists mainly of the crack initiation time. Consistently, non-aqueous liquids such as formamide, which are known (Michalske and S.W. Freiman, 1983) to cause slow crack growth in glass but do not initiate a sharp crack under a sub-critical stress (Hirao and Tomozawa, 1987b), were found to cause mechanical fatigue in freshly abraded glasses, but not in treated glasses with blunt crack tips (Tomozawa and Hirao, 1987a). It was found (Hirao and Tomozawa, 1987b; Tomozawa Hirao, 1987a; Wakabayashi and Tomozawa, 1988) that only water and ammonia are capable of initiating a sharp crack from a blunt crack under sub-critical stress, causing static fatigue failure for specimens with a blunt crack under sub-critical stress. The time required for crack initiation in water (and probably in ammonia) was found to be dependent on stress (Hirao and Tomozawa, 1987b). It was suggested that the unique ability of water and ammonia to cause crack initiation under a sub-critical stress is related to their ability to diffuse into glasses under stress (Wakabayashi and Tomozawa, 1988; Hirao and Tomozawa, 1987c).

Diffusion of water into glass is slow at room temperature but can be accelerated by stress (Nogami and Tomozawa, 1984). The most dramatic manifestation of stress accelerated diffusion of water into glass at room temperature is water entry into silica glass during microhardness indentation (Hirao and Tomozawa, 1987c; Tomozawa and Hirao, 1987b). Because of the water entry, the microhardness decreases with the indentation loading time when measured in water or in a water vapor-containing atmosphere, while the microhardness remains constant, independent of the indentation loading time, when measured in non-aqueous liquids such as toluene (Westbrook and Jorgenson, 1965). It is anticipated that similar time dependent hardness values would be observed when the microhardness indentation measurement is performed in ammonia.

In view of these observations, it was suggested that crack initiation in glasses involves stress-accelerated diffusion of water (or ammonia) into the glass specimen near the crack tip. The objective of this paper is to explore the process of crack initiation after water entry into the crack tip of glasses by examining some of the mechanical properties of glasses containing water.

Most of the observations described so far were made on silica glass and high silica glass but qualitatively similar trends are expected for other oxide glasses. Therefore, sodium silicate glasses with various water contents will be used since many properties of these glasses were previously investigated (Takata et al. 1981; Acocella et al., 1984; Tomozawa et al., 1983).

EXPERIMENTAL

Sodium trisilicate ($Na_2O \cdot 3SiO_2$) glasses with various water contents

were prepared by sealing the dry glass, with an appropriate amount of water, into a platinum tube and subjecting it to a high temperature and high pressure. The details of this method of specimen preparation were reported earlier (Takata et al., 1981; Acocella et al., 1984; Tomozawa et al., 1983). Specimens containing up to 9 wt % water were prepared by this method. For higher water content glass specimens, an alternative and less expensive method of drying a commercial soluble silicate was used. The latter method produced $Na_2O \cdot 3.3SiO_2$ glasses with water contents ranging between 15-25 wt %. These specimens were used earlier to study the mechanical fatigue in paraffin oil, in which no slow crack growth is expected to take place (Ito and Tomozawa, 1982b). It is assumed that the slight difference in the sodium oxide to silica ratio in specimens prepared by the two different methods has little influence on the various properties of the glasses.

The indentation microhardness was measured as a function of loading time in toluene, using a Vickers hardness tester (Model M-400, Akashi Works Co., Japan) at 100 g load. The part of the specimen where the diamond indenter made contact was covered with toluene, which was pretreated with a molecular sieve. The experimental method here is similar to that described earlier (Hirao and Tomozawa, 1987c).

RESULTS

The dynamic (steadily rising load) fatigue of the glasses tested here was investigated earlier (Ito and Tomozawa, 1982b) and is shown in Fig. 1. Dry $Na_2O \cdot 3.3SiO_2$ glass shows practically no dynamic fatigue while glasses containing large quantities of water show extensive fatigue. The near absence of fatigue in dry $Na_2O \cdot 3.3SiO_2$ glass is consistent with the view that paraffin oil is incapable of causing a slow crack growth or initiating a sharp crack under a sub-critical stress since it does not diffuse into glass. On the other hand glasses with a high water content show extensive fatigue even in paraffin oil, which does not cause slow crack growth nor time dependent crack initiation under a sub-critical stress for ordinary glasses. The observed mechanical fatigue, therefore, must come from the time dependent strength of the specimen itself rather than from the environmental effect on the strength. The corresponding effective Young's modulus value obtained from the stress-strain curve (Ito and Tomozawa, 1982b) is shown is Fig. 2. For specimens containing more than 20 wt % water, effective Young's modulus was found to be stress rate or time dependent. For glasses with less than 15 wt % water, however, effective Young's modulus was constant during the fatigue measurement.

The hardness of glasses decreases with increasing water content (Ito and Tomozawa, 1982b; Takata et al., 1982; Nogami and Tomozawa, 1983). Here, hardness was measured as a function of loading time as well as of water content. In Fig. 3, the time dependence of the Vickers indentation hardness measured in toluene under a 100 g load is shown for glasses with various water contents. Glass specimens with no added water show nearly time independent hardness, consistent with the previous results (Hirao and Tomozawa, 1987c; Westerbrook and Jorgenson, 1965). On the other hand, glass specimens with water show a decrease in hardness with loading time. This type of time dependent hardness has never been observed in toluene. Furthermore, this time dependence appears to become more pronounced for specimens with greater water contents.

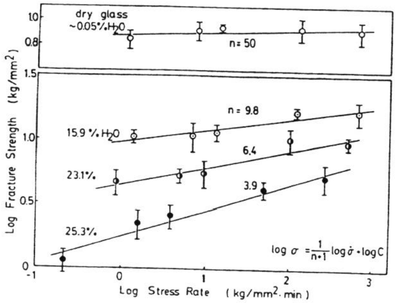

Fig. 1.

Fracture strength vs. stress rate for $Na_2O\cdot3.3SiO_2$ glasses with various water contents. (Measured in paraffin oil at room temperature; ± 1 standard deviation). (after Ito and Tomozawa, 1982b)

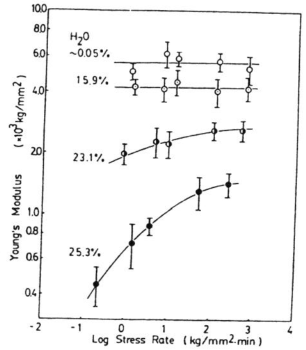

Fig. 2.

Apparent Young's Modulus vs. stress rate for $Na_2O\cdot3.3SiO_2$ glasses with various water contents, (± 1 standard deviation). (after Ito and Tomozawa, 1982b)

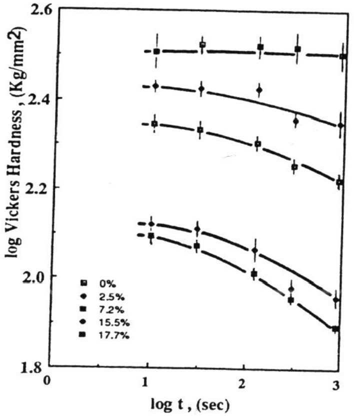

Fig. 3.

Loading time dependence of Vickers hardness measured under 100 g load in toluene for $Na_2O\cdot3SiO_2$ glasses with various water contents. (The two glasses with the highest water contents have the composition $Na_2O\cdot3.3SiO_2$).

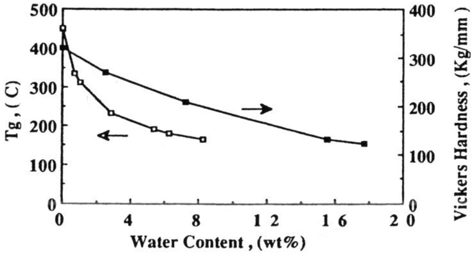

Fig. 4.

Comparison of the glass transition temperature, Tg, and Vickers hardness value measured in toluene under 100 g load for 10 s. for $Na_2O\cdot3SiO_2$ glasses with various water contents. (The two glasses with the highest water contents have the composition $Na_2O\cdot3.3SiO_2$).

Earlier, the glass transition temperatures of these glasses were measured (Tomozawa et al., 1983). The Vickers indentation hardness obtained in toluene under 100 g load for 10 s. duration is shown in Fig. 4, together with the glass transition temperature. The glass transition temperature corresponds to a viscosity of 10^{13} poise. It can be seen that there is a close analogy between the two measured quantities. A similar correlation between viscosity and hardness was reported earlier (Bastick, 1950).

The water in these high water content glasses can take the form of either hydroxyl water or molecular water. The fraction of each type of water, as determined by IR spectroscopy (Acocella et al, 1984), is shown in Fig. 5. Comparing this result with the glass transition temperature, and assuming that the glass transition temperature of the glasses with water is given by the weighted average of those of dry glass and water, it was suggested (Tomozawa et al., 1983) that the reduction of the glass transition temperature is primarily due to the hydroxyl water, while the molecular water simply diluted the glass structure. The similarity between the glass transition temperature and the hardness implied that the hardness reduction with increasing water content was also caused by the hydroxyl water.

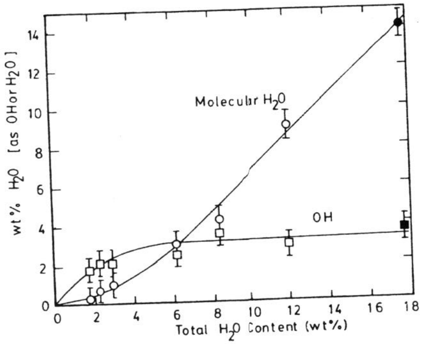

Fig. 5. Speciation of water in $Na_2O.3SiO_2$ glasses with various water contents. (The sample with the highest water content has the composition $Na_2O\cdot3.3SiO_2$).
(after Acocella et al., 1984)

DISCUSSION

There are two interpretations of the microhardness of glass. One is that the hardness is a measure of plastic deformation, similar to the case of metals. It is possible then to calculate the yield stress from the hardness value. For example, Johnson (1970) showed that the hardness, H, is given by

$$H = (2Y/3)\ [1 + \ln\ (E \tan \beta/3Y)] \tag{1}$$

where Y is the yield stress, E the Young's modulus, and β the inclination of the wedge face to the surface of the solid, 22 degrees for the case of the Vickers indenter. March (1964a, b) used a similar expression to obtain the yield stress of glasses from the indentation hardness and found that the yield stress was smaller than the theoretical cohesive strength of glass. He suggested, consequently, that the fracture of ordinary glasses involved plastic deformation near the crack tip. In this interpretation, the reduction of the microhardness with increasing water content can be attributed primarily to the reduction in the yield stress. Water apparently makes the plastic deformation easier. This interpretation is consistent with a phenomenon called hydrolytic weakening (Briggs and Blacic, 1984) observed in crystalline silica, in which yield stress is observed to decrease with water incorporation. It was reported (Aines and Rossman, 1984) that molecular water may be primarily responsible for the yield stress reduction. In addition, it appears that water in glass causes the yield stress of a glass to decrease with the loading time.

The other interpretation of the hardness of glasses is non-Newtonian viscous flow (Douglas, 1958). According to this model, when a glass is subjected to an increasing stress, viscosity decreases and a permanent deformation takes place, by non-Newtonian viscous flow, at or near a certain critical stress. During indentation, when the tip of the diamond indenter first touches the glass, stress is sufficiently high and the viscosity is low enough to allow the deformation of the glass. As the indentation size increases, the viscosity becomes high and further deformation becomes impossible near the critical stress. Phenomenologically, this critical stress is similar to the yield stress since a material exhibits a permanent deformation near that stress value. The analogy between the glass transition temperature at a constant viscosity of 10^{13} poise and the room temperature hardness (Fig. 4) appears to support this interpretation of hardness in terms of non-Newtonian viscous flow.

According to Griffith (1921), the fracture strength, σ_f, for plane stress is given by

$$\sigma_f = \sqrt{2E\gamma/\pi C}$$
$$= \sqrt{G_c E/\pi C} \qquad (2)$$

where γ is the fracture surface energy, G_c the critical strain energy release rate, which is equal to 2γ for a perfectly brittle material, and C the crack length. Several attempts were made to extend the Griffith's equation to materials which show permanent deformation before fracture. For example, Cottrell (1965) suggested the following expression:

$$G_c = 2YV(C)^* \qquad (3)$$

where $V(C)^*$ is the critical crack opening displacement at which the fracture occurs. The crack opening displacement is given, for a nearly brittle material, such as glass, by

$$V(C) = 4YR/\pi E \qquad (4)$$

where R is the length of the plastic deformation zone (Tetelman and McEvily, 1967). Although Griffith's equation (2) is the condition for crack growth, its extention, equation (3), is considered to be valid for the crack initiation, also (Tetelman and McEvily, 1967).

According to equation (3), it is expected that the fracture strength decreases with decreasing yield stress. In this expression, the yield stress does not have to be the onset of plastic deformation in which dislocation motion is involved. It can be interpreted more broadly as the critical stress at which permanent deformation starts. The present experimental data appear to be consistent with this expression, at least qualitatively, and the time dependent strength observed for the water-containing glasses in paraffin oil is considered to be caused predominantly by the time dependent yield stress. Glasses with high water content, because of their low viscosity, readily show blunting of their crack tips even at room temperature and equation (3) appears to account for the crack initiation of these glasses. For glasses containing more than 20 wt % water, effective Young's modulus was observed to decrease with decreasing stressing rate (Fig. 2) and consequently with increasing stressing time but, according to an expression by Cottrell, Young's modulus does not play a role in time dependent strength. The exact mechanism by which the yield stress decreases with the stressing time is not clear but it is possible that it is related to the structure of water in glass, especially the relative concentrations of hydroxyl water (Si-OH) and of molecular water (H_2O), and its variation with stress.

Although the present measurement is directly concerned with glasses containing large quantities of water, it is suggested that the present finding is applicable to the fatigue of some of the conventional oxide glasses, since water diffusion into glass near the crack tip at room temperature produces water-containing glasses, at least locally. In other words, it is suggested that the mechanical fatigue of some glasses with blunt crack tips takes place through water diffusion into the crack tips and the consequent time dependent yielding of the glass. When ordinary dry glass was indented in water or in a water vapor-containing atmosphere, the hardness was found (Tomozawa and Hirao 1987b) to decrease with time becuase of the water entry into the glass, but the amount of the water which entered the glass appeared to saturate quickly, suggesting that the observed decrease of the hardness during the prolonged indentation was due to the time dependent properties of the glass containing water rather than the time dependent entry of water into glass. The present view is somewhat similar to that by Marsh but in the present model the yield stress, which is important in the fracture process, is that of water-containing glasses instead of ordinary dry glasses.

CONCLUSION

According to a model which involves a permanent deformation of the crack tip, the fracture strength decreases with decreasing yield stress. It was found that water-containing glasses show a microhardness decreasing with indentation loading time. This can be interpreted as manifestation of the time dependent yield stress. It was suggested that the mechanical fatigue of some glass specimens, especially those with blunt crack tips, involves stress-accelerated water diffusion into the crack tip and time dependent yielding of the resulting water-containing glasses.

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