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PROGRESS REPORT

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entitled

MECHANISM OF MECHANICAL FATIGUE OF SILICA GLASS

prepared by, Dr. Minoru Tomozawa

Materials Engineering Department

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II. Research results obtained in the current program

Significant Accomplishments

1. Existence of a blunt crack tip.

Strength increase of abraded glasses by thermal and chemical treatments was found best explained by crack tip blunting.

2. Fatigue behavior of glasses with blunt cracks.

Fatigue of silica glass with blunt crack tips was found to involve crack initiation in addition to crack propagation, and only water and ammonia were found capable of causing crack initiation from blunt crack tips at sub-critical stresses.

3. Water entry into glass under stress.

Water was found to enter into silica glass during microhardness indentation as well as during slow crack growth in water-containing atmospheres at room temperature.

4. Water diffusion into SiO_2 glass at low temperature.

Water diffusion into silica glass at low temperature showed anomalous phenomena including initial time dependences of solubility and apparent diffusion coefficient. These were explained by the slow reaction between silica and water in glass.

5. Role of water in glass.

Glass containing water showed greater fatigue susceptibility and lower crack initiation stress than dry glass.

6. Cyclic fatigue.

Fatigue of abraded silica glass showed effects of cyclic stress when tested by the rotation bending method while no cyclic stress effect was observed in reciprocal bending.

7. Fatigue resistance improvement by coating.

A new coating which can reduce fatigue of silica glass was developed.

List of publication in the current program

1. M. Tomozawa, K. Hirao and P. E. Bean "Origin of Strength Increase of Abraded or Indented Glass upon Annealing", J. Am. Ceram. Soc., **69** [8] C186-C187 (1986).
2. K. Hirao and M. Tomozawa "Kinetics of Crack Tip blunting of Glasses", J. Am. Ceram. Soc., **70** [1] 43-48 (1987).
3. K. Hirao and M. Tomozawa "Dynamic Fatigue of Treated High-Silica Glass; Explanation by Crack Tip Blunting", J. Am. Ceram. Soc., **70** [6] 377-82 (1987).
4. M. Tomozawa and K. Hirao, "Mechanical Fatigue of Silica Glass", J. Non-crystalline Solids, **95/96**, 149-160 (1987).
5. K. Hirao and M. Tomozawa, "Microhardness of SiO_2 Glass in Various Environments", J. Am. Ceram. Soc., **70** [7] 497-502 (1987).
6. M. Tomozawa and K. Hirao, "Diffusion of Water into Oxides during Microhardness Indentation", J. Mat. Sci. Letters, **6** [7] 867-868 (1987).
7. H. Wakabayashi and M. Tomozawa, "Static Fatigue of SiO_2 Glass in Ammonia", J. Non-Crystalline Solids, **102**, 95-99 (1988). (Appendix I)
8. M. Tomozawa, "The Role of Water in Mechanical Fatigue of Glasses", p.1563-70 in Advances in Fracture Research. Proceedings of the 7th International Conferences on Fracture (ICF7), Houston, Texas March 20-24, 1989. (Appendix II)
9. W.-T. Han and M. Tomozawa, "Mechanism of Mechanical Strength Increase of Soda-lime Glass by Aging", J. Am. Ceram. Soc., **72**, [10] 1837-43 (1989). (Appendix III)

10. W.-T. Han and M. Tomozawa, "Reply to Comments on Mechanism of Mechanical Strength Increase of Soda-Lime Glass by Aging", J. Am. Ceram. Soc., **93** [5] 1464-65 (1990).

11. H. Wakabayashi and M. Tomozawa, "Diffusion of Water into SiO_2 Glass at Low Temperature", J. Am. Ceram. Soc., **72**, [10] 1850-55 (1989). (Appendix IV)

12. W.-T. Han and M. Tomozawa, "Crack Initiation and Mechanical Fatigue of Silica Glass", J. Non-Crystalline Solids, **122**, 90-100 (1990). (Appendix V)

13. W.-T. Han and M. Tomozawa, "Indentation Creep of $Na_2O \cdot 3SiO_2$ Glasses with Various Water Contents", to appear in J. Am. Ceram. Soc. (Appendix VI)

14. W.-T. Han and M. Tomozawa, "Effect of Residual Water in Silica Glass on Static Fatigue" to appear in J. Non-Crystalline Solids.

15. M. Tomozawa, W.-T. Han and W.A. Lanford, "Water Entry into SiO_2 Glass During Slow Crack Growth" Submitted to J. Am. Cerm. Soc.(Appendix VII).

Discussion of obtained results

1. Existence of a blunt crack tip.

The issue of blunt crack tips was examined first. It is well recognized that the mechanical strength of freshly abraded or indented glass increases upon heat-treatment or hot water-treatment. Two explanations were offered for this phenomenon; the reduction of the stress concentration due to crack tip blunting[57] and the release of the residual tensile stress[17,20] which existed near the crack tip.

It was shown[16,23] that the strength increase upon heat-treatment at the annealing temperature can not be attributed to residual stress release but can best be explained by crack tip blunting caused by the viscous flow of the glass surface facilitated by water diffused into the glass from the atmosphere. One of the evidences for this conclusion was that annealing in vacuum of abraded glasses did not produce appreciable strengthening even though residual stress can be released by this procedure. Earlier, it was shown that the strength increase caused by hot water treatment was due to crack tip blunting caused by the dissolution and reprecipitation of glass at the crack tip[18,19]. This process of strengthening by hot water treatment was extended to a higher temperature (200°C) using a hydrothermal unit. As much as 100% strengthening was achieved by this process while no change in crack length took place. It is not possible to obtain this much strengthening of abraded and aged samples by residual stress release. Glass samples with sharp macro-cracks also showed similar strengthening even though there can be no residual stress in this case. These results confirm that the tips of cracks in glass can be made blunt.

Strength increase of abraded soda-lime glass observed after soaking in room temperature water was also attributed to a similar mechanism. In this case, it is proposed that ion-exchange between alkali in glass and hydrogen (or hydronium) produces a weak surface layer at the crack tip thus effectively blunting the tip[58]. A recent study[59] of the glass strength by biaxial stressing appears to support the crack tip blunting model.

2. Fatigue behavior of glasses with blunt cracks.

Both dynamic fatigue[21], fatigue under steadily increasing stress, and static fatigue[22,23], fatigue under a constant stress, of high silica glass and silica glass[60] were measured for freshly abraded glass samples with sharp crack tips and treated glass samples with blunt crack tips in various environments. It was found that the fatigue behavior of the freshly abraded glasses can be explained by the slow crack growth mechanism while that of the treated glasses with blunt cracks required the assumption that crack initiation plays an important role. In addition, analysis showed that only water and ammonia can cause crack initiation at subcritical stress. Equivalently, the glasses with blunt cracks showed static fatigue in water and in ammonia but not in other chemicals.

3. Water entry into glass under stress.

In order to understand the crack initiation process in glass, the behavior of glass under stress before a crack initiates was investigated using a microhardness indenter[24,25]. It was found that the crack initiation behavior correlates well with the hardness of the glass; both crack initiation load and hardness were time dependent in water, while both quantities were time independent in liquids such as formamide and hydrazine. Thus, crack initiation at a sub-critical stress appears to be related to the time dependent hardness. It was found that the time dependent hardness observed in air and water was caused by the entry of water into glass under stress[24,25].

In related research[26] on defects in silica glass, it was found that point defects are produced below the surface of silica glass powder produced in a water-free environment, while no defects were detected in powder produced in a water-containing atmosphere. This difference appears to originate from the water entry into silica glass during fracture in water-containing atmospheres.

Recently, extending these works, it was found that water enters into silica glass during slow crack growth in water-containing atmospheres. This was demonstrated by measuring the hydrogen depth profile of a fractured surface by a nuclear resonance technique. Hydrogen (from water) was observed to exist both on the glass surface as an adsorption layer and also within a few hundred angstrom thick surface layer when the fracture surface was produced by slow crack growth in water-containing atmospheres. The hydrogen concentration profile was also a function of stress intensity (or crack velocity), the concentration being greater under lower stress intensity (or slower crack velocity).

4. Diffusion of water into SiO_2 glass at low temperature.

In order to establish the reference value for water entry into silica glass under stress, the low temperature diffusion of water into SiO_2 glass was investigated[29] using an FTIR. Several anomalous phenomena were found at low temperatures. The diffusion process at low temperatures was non-Fickian at first; the apparent diffusion coefficient decreased and the surface concentration increased with time at a constant temperature under a constant water vapor pressure.

The steady state diffusion coefficient at low temperatures was higher than that obtained by extrapolation from higher temperatures. In addition, the activation energy for diffusion at low temperatures was lower than that at high temperatures. The infra-red absorption spectra of water in glass were also different; the absorption peak produced at lower temperatures shifted to lower wave numbers indicating a greater interaction between hydroxyl pairs, e.g. in the form of hydrogen bonding or molecular water. The observed time dependent phenomena were attributed to the slow kinetics of reaction between water in glass and the glass network. The lower activation energy of the steady state diffusion coefficient was attributed to a shift in equilibrium between hydroxyl and molecular water caused by high stress at low temperatures. Recent observation[61] of the water absorption peak in silica shifting to lower wave numbers under high hydrostatic stress appears to be consistent with this view.

5. Role of water in glass.

In order to learn the role of water which entered into the glass under stress, mechanical properties of glasses containing water were investigated. Earlier, it was shown that fatigue susceptibility increased with increasing water content for sodium silicate glasses[33]. Recently, microhardness indentation of sodium silicate glasses with various water contents was investigated[34]. It was found that glasses containing water showed indentation creep even in toluene, while dry glasses did not. This is consistent with the earlier finding that the indentation creep of dry glasses in water-containing atmospheres is due to water entry into glass under stress. It is possible that the time dependent reaction between molecular water in glass and glass under stress is causing the time dependent hardness observed in toluene.

Under high indentation load, all glasses showed time dependent hardness even in toluene[36]. This time dependent hardness was attributed to inhomogeneous non-Newtonian flow. This is phenomenologically similar to plastic deformation. Water in glass appears to decrease the onset stress for the inhomogeneous non-Newtonian flow or yield stress.

Silica glasses which were heat-treated at different temperatures showed different fatigue behavior[35]. This was attributed to the different crack initiation stress as a result of different amounts of water remaining in the glasses. These observations, together with work[37] by other investigators, show clearly that water in glass increases the fatigue susceptibility of glasses by promoting crack initiation and crack growth.

6. Cyclic Fatigue.

Cyclic fatigue tests of abraded dry silica glass were conducted by two different methods; a reciprocal bending method and a rotational bending method. It was found that by the former method, cyclic fatigue tests did not show any detrimental effect compared with static fatigue tests, while by the latter method, the life time was much shorter compared with static fatigue (cf. Figures 3(a) and 3(b)). This finding is qualitatively similar to the preliminary work by Proctor[62]. The shorter fatigue life by rotation bending was attributed to the widening, in addition to deepening of the flaw, due to the stressing condition during rotation and increased stress intensity at the depth of the flaw. The absence of the normal (reciprocal bending) cyclic effect on crack growth is consistent with the earlier analysis by Evans[53]. Cyclic fatigue tests of silica glass specimens with blunt crack tips are under way.

7. Fatigue Resistance Improvement by Coating.

Our study on water diffusion into silica glass at low temperatures suggested an interesting possibility for reducing water diffusion into and mechanical fatigue of silica glass. At low temperatures, the rate of reaction between molecular water and silica glass appears to be slow, and molecular water can diffuse faster being trapped (converted to immobile hydroxyl) less frequently compared with the phenomenon at high temperatures. If one could coat the silica glass with a material which can trap molecular water more effectively than silica glass, this coating material would work as a water diffusion barrier. Coating materials for silica glass optical waveguides[63,64] recently developed by industry, carbon and titania-silicate, appear to have this desired high trapping efficiency. Using this idea a new, potentially more effective coating than carbon or titania-silicate, was developed (cf. Figure 4). Use of this material in production of optical fiber at a U.S. industry is under consideration.

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