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Mechanism of Mechanical Fatigue of Silica Glass

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Abstract

The objective of the proposed research was to clarify the static fatigue mechanism of silica glasses such as optical communication fibers.

The most popular explanation of static fatigue is a slow growth of a surface crack by the stress corrosion reaction between water and glass at the crack tip. The exact nature of the corrosion reaction, however, is not clear. The adsorption of water molecules from the atmosphere on the tip of a sharp crack was considered by some to cause the observed strength degradation.

First, the possible presence of blunt crack tips was investigated. Some researchers have maintained that the crack tip of a brittle material such as glass remains atomistically sharp and the observed strength increase of an unstressed glass by thermal or hydrothermal treatment is due to the reduction of the residual tensile stress near the crack. We have shown that the strength increase by thermal or hydrothermal treatment can best be explained by the formation of blunt crack tips. One of the reasons which favor the blunt crack hypothesis is that the extent of strengthening by hydrothermal treatment exceeds the strengthening possible by the removal of the residual stress. Glasses with blunt cracks were found to exhibit different fatigue behavior from those with sharp cracks. While specimens with sharp cracks can exhibit fatigue in both water and non-aqueous liquid such as formamide and hydrazine, specimens with blunt cracks exhibited fatigue only in water (and ammonia). Non-aqueous liquids can be adsorbed on the glass surface but can not be absorbed in the glass while water can exhibit both adsorption and absorption (or diffusion). The observed mechanical behavior can be explained as follows: While the fatigue of glasses with sharp cracks involves only crack propagation, that of glasses with blunt cracks involves both crack initiation and propagation. Non-aqueous liquids can aid the crack propagation but can not help initiate a crack. On the other hand, water (and ammonia) can do both. The ability of water to initiate a crack appears related to its diffusion into the glass. The present observation of this crack initiation of specimens with blunt cracks is probably analogous to conditions in pristine, flaw-free glasses such as optical fibers. The mechanical fatigue of pristine silica fibers takes place in water but is not expected in non-aqueous liquids. Water entry into silica glass was found to be accelerated by an applied stress.

Details of the water entry (or diffusion) into silica glasses at low temperature were examined. The water entry into silica glasses at low temperatures was found closely coupled with the structural relaxation of the glass. The structural relaxation at low temperatures lowers the fictive temperature of the glass and, in the case of silica glass, causes a volume expansion and an increase in the average Si-O-Si bond angle, the same structural changes expected under a tensile stress. Water entry into a silica glass promotes the structural relaxation and the structural relaxation in turn affects the water solubility and diffusion. It was found that the structural relaxation can be monitored by following the shift of peaks of silica structural bands caused by the Si-O-Si bond angle change. This observation led to a simple IR spectroscopic method of measuring the fictive temperature of glasses. IR absorbance measurements give a fictive temperature averaged over the entire specimen thickness while the IR reflection measurements give a fictive temperature of the specimen surface. By combining IR reflection peak position measurement and successive etching of the specimen, it became possible to determine the depth profile of the fictive temperature. This type of distribution in fictive temperature was observed in a communication fiber and in a specimen heat-treated at a temperature lower than the glass transition temperature.

It was found that the fictive temperature of a glass has a strong influence on fatigue behavior, with glasses with higher fictive temperatures exhibiting greater fatigue resistance.

I. Introduction

Glasses exhibit static fatigue[1], a strength degradation under a static load in the presence of water or water vapor. This could limit the service life of a glass product and would be a great concern when a long design life of a glass product is intended. For example, the service life of optical waveguides can be limited by static fatigue. The fatigue life depends upon the applied stress, lower stresses giving longer lifetimes. Once a failure time vs. load relationship, (a fatigue curve), is established, the maximum load can be specified in order to obtain a desired lifetime. But it is not practical to establish fatigue curves for a long period of time e.g. forty years. The desirable alternative would be to understand the phenomenon of static fatigue and represent it by a theory which can cover a wide range of the fatigue life.

It is well known that the glass-water interaction is responsible for the mechanical fatigue. The stress corrosion theory by Charles-Hillig[2,3] is a popular theory but the exact nature of the corrosion reaction is not clear. It was suggested[4] that the adsorption of water on the crack tip surface promotes the crack propagation which can lead to mechanical failure. But even a pristine glass fiber without any surface cracks[5] appears to exhibit mechanical fatigue. In this case, before a crack can propagate, it must be initiated. While many non-aqueous liquids appear to be able to promote crack propagation, only water appears to be capable of initiating cracks. This ability of water appears related to its ability to enter into the glass. Details of water entry into silica glasses were investigated.

II. Significant accomplishments in the current program

1). Existence of a blunt crack tip.

The strength increase of abraded glasses by thermal, chemical, and hydrothermal treatments was found to be best explained by crack tip blunting.

2). Mechanical behavior of glasses with blunt cracks.

The fatigue of a silica glass with blunt cracks was found to involve crack initiation in addition to crack propagation, and only water and ammonia were found to be capable of causing crack initiation from blunt cracks at sub-critical stresses. Furthermore, the apparent fracture toughness was much higher for silica glasses with blunt cracks than those with sharp cracks. Correspondingly, the mirror constant, which is normally considered to be a material constant, was found to increase with the estimated crack tip radius.

3). Water entry into glass under stress.

Water was found to enter into a silica glass during microhardness indentations as well as during slow crack growth in water-containing atmospheres at room temperature. The effects of applied stresses on the water diffusion into silica glasses were re-examined. At low temperatures, tensile stresses were found to accelerate the diffusion coefficient.

4). Water diffusion into SiO_2 glass at low temperature.

Water diffusion into silica glass at low temperatures showed anomalous features including an initial time dependence of solubility and diffusion coefficient. It was found that these anomalous features are related to the time dependent relaxation of the glass structure. This was shown by measuring the shift of the IR peak at 1873 cm^{-1}, which is an indirect measure of the Si-O-Si bond angle change. The time dependent anomalous diffusion behavior was observed when the rate of the structural relaxation lags behind the rate of water diffusion.

5). Mechanical properties of glasses with high water concentration.

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

6). Cyclic fatigue.

The fatigue of an abraded silica glass showed effects of the 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 SiO coating on abraded silica glass was found to reduce mechanical fatigue.

8). IR peak assignments for the silica-water system.

IR peaks of SiO_2 glasses with H_2O were investigated and assigned. Also, molecular water was found to be present in silica glasses after low temperature hydration experiments.

9). Water diffusion and structural changes in silica glasses.

At high temperatures, the rates of both structural relaxation of a silica glass and oxygen vacancy disappearance of oxygen-deficient silica glasses exposed to water vapor were faster than the rate of water diffusion itself. This indicates that a minor fraction of water is diffusing faster, unrestricted by the chemical equilibrium, than the majority portion which is restricted.

10). Effect of nitrogen and carbon implantation on devitrification of silica glasses.

The crystal growth rate was decreased when nitrogen was implanted in oxygen deficient silica glasses but not in stoichiometric silica glasses. It was suggested that the oxynitride bonds which formed in the surface layer reduced the water diffusion and diffusion-controlled crystal growth rate.

11) Simple IR spectroscopic method of determining the fictive temperature of glasses.

It was found that IR peak positions of silica structural bands are related to the fictive temperature of the glass. The fictive temperature can be determined by simply measuring the peak position.

III. 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-Cryst. 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, "Effect of Ammonia on Static Fatigue of SiO_2 Glass", J. Non-Cryst. Solids, 102, 95-99 (1988).
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.
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).
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).
12. W.-T. Han and M. Tomozawa, "Crack Initiation and Mechanical Fatigue of Silica Glass", J. Non-Cryst. Solids, 122, 90-100 (1990).
13. W.-T. Han and M. Tomozawa, "Indentation Creep of $Na_2O{\cdot}3SiO_2$ Glasses with Various Water Contents", J. Am. Ceram. Soc., 73, 3626-32 (1990).
14. W.-T. Han and M. Tomozawa, "Effect of Residual Water in Silica Glass on Static Fatigue" J. Non-Cryst. Solids, 129, 97-104 (1990).
15. M. Tomozawa, W.-T. Han and W.A. Lanford, "Water Entry into SiO_2 Glass During Slow Crack Growth", J. Am. Ceram. Soc., 74, 2573-76 (1991).
16. W.-T. Han and M. Tomozawa, "Strengthening of Abraded Silica Glass by Hydrothermal Treatment", Ceramic Transactions vol.20, 183-190 (1991). Ed. by K.M. Nair, The American Ceramic Society.
17. M. Tomozawa, W.-T. Han and K.M. Davis, "Fatigue Resistant Coating of SiO_2 Glass" SPIE, vol.1590, 160-167 (1992).
18. W.-T. Han and M. Tomozawa, "Fractographic Analysis of Hydrothermally-Treated Silica Glass", J. Non-Cryst. Solids, 163, 309-314 (1993).
19. A. Agarwal, M. Tomozawa and W.A. Lanford, "The Effect of Stress on Water Diffusion in Silica Glass at Various Temperatures", J. Non-Cryst. Solids, 167,139-148 (1994).
20. H. Li, M. Tomozawa and V. Lou "Effect of Nitrogen and Carbon Implantation on Devitrification of Silica Glasses" J. Non-Cryst. Solids, 168, 56-63 (1994).
21. H. Li and M. Tomozawa, "Mechanical Strength Increase of Abraded Silica Glass by High Pressure Water Vapor Treatment", J. Non-Cryst. Solids, 168, 287-292 (1994).
22. M. Tomozawa, H. Li and K.M. Davis, "Water Diffusion, Oxygen Vacancy Annihilation, and Structural Relaxation in Silica Glasses" J. Non-Cryst. Solids, 179, 162-169 (1994).

23. K. Davis and M. Tomozawa, "Water Diffusion into Silica Glass", Diffusion in Amorphous Materials Eds. H. Jain and D. Gupta, TMS, Warrendale, PA. pp. 119-127 (1994).
24. K. Davis and M. Tomozawa, "Diffusion into Silica Glass: Structural Changes in Silica Glass and their Effect on Water Solubility and Diffusivity", J. Non-Crystalline Solids, 185, 203-220 (1995).
25. A. Agarwal, K.M. Davis and M. Tomozawa, "A Simple IR Spectroscopic Method for Determining Fictive Temperature of Silica Glasses", J. Non-Cryst. Solids, 185, 191-198 (1995).
26. H. Li, A. Agarwal and M. Tomozawa, "Effects of Fictive Temperature on Dynamic Fatigue Behavior of Silica and Soda-Lime Glasses", J. Am. Ceram. Soc., 78, 1393-96 (1995).
27. A. Agarwal and M. Tomozawa, "Determination of Fictive Temperature of Soda-Lime Silicate Glass" J. Am. Ceram. Soc. 78, 827-829 (1995).
28. K.M. Davis and M. Tomozawa, "An Infrared Spectroscopic Study of Water-Related Species in Silica Glasses", submitted to J. Non-Cryst. Solids (1995).
29. A. Agarwal and M. Tomozawa, "Correlation of Silica Glass Properties with the Infrared Spectra" to be submitted to J. Non-Cryst. Solids (1995).
30. A. Agarwal and M. Tomozawa, "Effects of Water on Kinetics of Structural Relaxation of Silica Glass", to be submitted to J. Non-Cryst. Solids (1995).

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V. 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 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[6] and the release of the residual tensile stress[7,8] which existed near the crack tip. It was shown[9,10] 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 that diffused into the glass from the atmosphere. One piece of evidence 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. It was shown that the strength increase caused by hot water treatment was due to crack tip blunting caused by the dissolution and re-precipitation of glass at the crack tip[11,12]. This process of strengthening by hot water treatment was extended to higher temperatures (in 200°C water and in 250°C saturated water vapor) using a hydrothermal unit. As much as 200% 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 observations can be best explained by crack tip blunting rather than by the release of residual stress.

An alternative mechanism of strengthening by hot water treatment was suggested for soda-lime glasses. Namely a glass-water reaction product precipitates behind a crack forming a bridge but leaving the original crack tip intact[13]. This mechanism is similar to the dissolution and precipitation mechanism suggested for silica glass crack tip blunting. The only differences are the location of the precipitate, behind the crack tip vs. at the crack tip, and the precipitate composition. Near the crack tip, silica glass is expected to have the lowest solubility in water because of the tip curvature and precipitation is expected to take place most readily there. Furthermore, the precipitate composition in silica glass is expected to be nearly pure silica. In contrast, the composition of any precipitate in the crack tips of soda-lime glass is expected to be different from that of the glass. When a precipitate with the same composition as the glass forms at the crack tip the distinction between crack tip blunting and crack bridging disappears. Also, there are people who prefer to define a crack as having a sharp tip in distinction to all others as flaws. If this definition is followed, then one should say that a crack is turned into a flaw by thermal and hydrothermal treatments. In either case, the important point is that thermal and hot water treatments can make the abraded silica glasses stronger without shortening the length of the crack.

2). Mechanical behavior of glasses with flaws or blunt cracks.

Both dynamic fatigue[14], fatigue under steadily increasing stress, and static fatigue[10,15,16], fatigue under a constant stress, of high silica glass and silica glass 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 requires the assumption that crack initiation plays an important role. In addition, experiments 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. The mechanical fatigue behavior of these glass samples with blunt cracks is also expected to be closer to that of pristine silica optical fibers than that of freshly abraded silica glasses.

Increases in both fracture toughness and mirror constant were also observed[10,17] for the hydrothermally treated samples, even though these quantities are considered to be constants for a given material. Fracture toughness is usually obtained by multiplying the fracture strength of a sample by the square root of the crack length. Since hydrothermally treated glass samples with blunt crack tips have a higher mechanical strength with unchanged crack length, their fracture toughness was higher than freshly abraded silica glass samples. On the fracture surface of a glass, the crack origin is surrounded by a smooth zone called the mirror region, which is in turn bounded by rougher regions called mist and hackle. The size of the mirror region is a function of fracture strength and the product of the fracture strength and the mirror radius is known as the mirror constant, believed to be a unique constant for a given glass composition. For hydrothermally treated silica glasses, the mirror constant increased with increasing extent of crack tip blunting. Apparently, in order to obtain a constant fracture toughness and mirror constant, the crack tip must be sharp.

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[18,19]. It was found that the crack initiation behavior correlates well with the hardness of the glass. In addition, 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[18,19]. In related research[20] 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. Extending these works, it was found[21] 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 reaction 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.

4). Water Diffusion into SiO_2 glass at low temperature.

In order to establish the reference value for water entry into silica glass under stress, a diffusion study of water into SiO_2 glass was extended to lower temperatures[22,23] than most published works using an FTIR. Above ~850°C, many different silica glasses exhibited almost identical diffusion behavior, while below 850°C, a clear difference was observed for different silica glasses. In addition, several anomalous phenomena were found at temperatures lower than ~850°C such as the surface concentration increasing and apparent diffusion coefficient decreasing with time. The infra-red absorption spectra of water in glass were also different; the absorption produced at lower temperatures exhibited additional lower wave number peaks indicating the presence of hydrogen bonded hydroxyl and molecular water. In addition, water entry into silica glass promotes local structural relaxation as indicated by a shift of the IR peak at 1873 cm^{-1} due to Si-O-Si vibrations. Different water diffusion behavior above and below ~850°C appears to be related to the relative rate of water diffusion and structural relaxation: Above ~850°C, the rate of this structural relaxation is faster than the rate of water diffusion and water is diffusing in a relaxed (equilibrium) structure, while below ~850°C, the rate of this structural relaxation was slower than water entry and water is diffusing in a (time dependent) relaxing structure. The observed time dependent phenomena at lower temperatures were attributed to the slow rate of relaxation which affects kinetics of reaction between water in glass and the glass network as well as solubility.

5). Mechanical properties of glasses with high water concentrations.

In order to learn the role of water which enters into 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[24]. Further, microhardness indentation of sodium silicate glasses with various water contents was investigated[25]. 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 the glass under stress. It is possible that a time dependent reaction between molecular water in the glass and the glass network under stress is causing the time dependent hardness observed in toluene. Under high indentation load, all glasses including dry glasses showed time dependent hardness in toluene[26]. 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 after hydrothermal treatment showed different fatigue behavior[27]. This was attributed to different crack initiation stresses as a result of different amounts of water remaining in the glasses. These observations, together with work[28] by other investigators, show clearly that water in glass increases the fatigue susceptibility of glass by promoting crack initiation and crack growth.

6). Cyclic Fatigue.

Cyclic fatigue tests of abraded dry silica glass were conducted by two different methods including a reciprocal bending method and a rotational bending method. It was found that by the first 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. This finding is qualitatively similar to the preliminary work by Proctor[29]. The shorter fatigue life by rotation bending was attributed to the widening, in addition to deepening of the flaw, due to the time dependent stressing condition during rotation and increased stress intensity at various locations of the crack tip. The absence of the normal (reciprocal bending) cyclic effect on crack growth is consistent with the earlier analysis by Evans[30].

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 farther as it is trapped (converted to immobile hydroxyl) less frequently than in the case at high temperatures where the local reaction equilibrium is established instantaneously. If one could coat silica glass with a material which can trap molecular water more effectively than silica glass itself, this coating material would work as a water diffusion barrier. Coating materials for silica glass optical waveguides[31,32] recently developed by industry, including carbon and titania-silicate, appear to have this desired high trapping efficiency. Using this idea an SiO coating was applied to the surface of abraded silica glass and was found[33] to be effective in reducing static fatigue.

8). IR peak assignments for the silica-water system.

IR peaks of wet and dry SiO_2 glasses were investigated[23,34] and assigned. In particular, molecular water bands were analyzed in detail. This made it possible to determine the relative amounts of molecular water in silica glasses hydrated at low temperatures. It was found[23,34] that under a constant water vapor pressure, the amount of molecular water relative to hydroxyl water increased with decreasing treatment temperatures.

9). Water diffusion and structural changes in silica glasses.

At high temperatures, above ~850°C, rates of both structural relaxation indicated by the shift of an IR absorption peak at 1873 cm^{-1} due to Si-O-Si vibrations and oxygen vacancy disappearance of oxygen-deficient silica glasses exposed to water vapor were faster[35] than the rate of water diffusion itself. At high temperatures, it is usually assumed that the water-glass network reaction is fast and that a local equilibrium is established between the reactants and product instantaneously. The present observation indicates that a minor fraction of water is diffusing faster, unrestricted by the chemical equilibrium, than the majority fraction, which is restricted.

10). Effect of nitrogen and carbon implantation on devitrification of silica glasses.

The crystal growth rate decreased[36] when nitrogen was implanted in oxygen deficient silica glasses, while it was unaffected by ion-implantation in stoichiometric silica glass. It was suggested that the oxynitride bonding which formed in the surface layer reduced the water diffusion and diffusion-controlled crystal growth rates.

11) Simple IR spectroscopic method of determining the fictive temperature of glasses.

The peak portions of the IR structural bands due to Si-O-Si vibration, such as the fundamental peak at ~1200 cm^{-1}, an overtone at ~2260 cm^{-1} and a combination band at 1870 cm^{-1}, are uniquely related to the fictive temperature of the glass. Thus the fictive temperature of a glass can be determined simply be measuring the peak positions of these peaks and comparing with a pre-determined master curve relating the peak position and the fictive temperature[37,38]. The absorbance of the ~1200 cm^{-1} peak for silica is so intense that the reflection mode is used while the absorbance mode is used for the other two peaks. With the reflection mode a thin surface layer is probed while with the absorption mode, the entire thickness of the specimen is probed. By combining the reflection measurement with the successive etching of the surface layer it became possible to determine the fictive temperature as a function of the depth of the specimen when there is a distribution in the fictive temperature. The surface layer of the communication fiber, for example, appears to have a higher fictive temperature than the interior of the silica fiber.

12) Effects of fictive temperature on mechanical fatigue of glasses.

It was found that the fictive temperatures of silica and soda-lime glasses have a large influence on mechanical properties. Both fatigue resistance and fracture toughness of the glasses increased with increasing fictive temperature[39]. This fact has to be taken into account in order to explain the fatigue behavior of silica glass communication fiber.

References

1. B.A. Proctor, F. Whitney and J.W. Johnson, Proc. Roy. Soc. A. 297, 534 (1966).
2. R.J. Charles and W.B. Hillig, p.511 in Symposium on Mechanical Strength of Glass and Ways of Improving It, Union Scientifique Continentale du Verre. Charleroi, Bergium (1962).
3. W. B. Hillig and R. J. Charles, Stress Corrosion, p.682 in High Strength Materials, ed. V. F. Zackey, J. Wiley & Sons, New York, (1965).
4. T. A. Michaleske and S. W. Freiman, J. Am. Ceram. Soc., 66, 284 (1983).
5. C. R. Kurkjian and U.C. Peak, Appl. Phys. Lett., 42, 251 (1983).
6. R. E. Mould, J. Am. Ceram. Soc., 43, 160 (1960).

7. D.B. Marshall and B.R. Lawn, p.171 in Strength of Inorganic Glass. ed. C.R. Kurkjian, Plenum Oress, New York (1985).
8. B.R. Lawn, K. Jakau and A.C. Gonzalez, J. Am. Ceram. Soc., 67, C-36 (1984).
9. K. Hirao and M. Tomozawa, J. Am. Ceram. Soc., 70, 43 (1987).
10. W.-T. Han and M. Tomozawa, p.183 in Glasses for Electronic Applications, Ceramic Transactions, v.20, ed. K.M. Nair, The American Ceramic Society, Westerville, OH (1991).
11. S. Ito and M. Tomozawa, J. Am. Ceram. Soc., 65, 368 (1982).
12. Y. Bando, S. Ito and M. Tomozawa, J. Am. Ceram. Soc., 67, C-36 (1984).
13. D.H. Roach, S. Lathabaland and B.R. Lawn, J. Am. Ceram. Soc., 71, 97 (1988).
14. W.-T. Han, and M. Tomozawa, J. Non-Cryst. Solids, 122, 90 (1990)
15. H. Wakabayashi and M. Tomozawa, J. Non-Cryst. Solids, 102, 95 (1988).
16. M. Tomozawa and K. Hirao, J. Non-Cryst. Solids, 95/96, 149 (1987).
17. W.-T. Han and M. Tomozawa, J. Non-Cryst. Solids, 163, 309-314 (1993).
18. K. Hirao and M. Tomozawa, J. Am. Ceram. Soc., 70, 497 (1987).
19. M. Tomozawa and K. Hirao, J. Mat. Sci., 6, 867 (1987).
20. K. Kokura, M. Tomozawa and R.K. MacCrone, J. Non-Cryst. Solids, 111, 269 (1989).
21. M. Tomozawa, W.-T. Han and W.A. Lanford, J. Am. Ceram. Soc., 74, 2573 (1991).
22. H. Wakabayashi and M. Tomozawa, J. Am. Ceram. Soc, 72, 1850 (1989).
23. K.M. Davis, Ph. D. Thesis, Rensselaer Polytechnic Institute (1994). andK. Davis and M. Tomozawa, "Diffusion into Silica Glass: Structural Changes in Silica Glass and their Effect on Water Solubility and Diffusivity", J. Non-Crystalline Solids, 185, 203-220 (1995).
24. S. Ito and M. Tomozawa, J. de. Phys., 43, C9-611 (1982).
25. M. Tomozawa, p.1563 in Advances in Fracture Research, Proceedings of the 7th International Conferences on Fracture (ICF7), Houston, Texas, March 20-24, 1989.
26. W.-T. Han and M. Tomozawa, J. Am. Ceram. Soc. 73, 3626 (1990).
27. W.-T. Han, ans M. Tomozawa, J. Non-Cryst. Solids. 127, 97 (1991).
28. J.D. Schnapp, Silikattechnik, 37, 401 (1986).
29. B. A. Proctor, Nature, 210, 730 (1960).
30. A. G. Evans, Int. J. Fracture, 16, 485 (1980).
31. K.E. Lu, G.S. Glaesemann, R.V. Vanderwoestine and G. Kar, J. Lightwave Technol., 6, 240 (1988).
32. C.R. Kurkjian, J.T. Krause and M.T. Mattewson, J. Lightwave Technol., 7, 1360 (1989).
33. M. Tomozawa, W.-T. Han and K.M. Davis, SPIE vol.1590, 160-167 (1992).
34. K.M. Davis and M. Tomozawa, "An Infrared Spectroscopic Study of Water-Related Species in Silica Glasses" submitted to J. Non-Cryst. Solids. (1995).
35. M. Tomozawa, H. Li and K.M. Davis,J. Non-Cryst. Solids, 179, 162-169 (1994).
36. H. Li, M. Tomozawa and V. Lou, J. Non-Cryst. Solids. 168, 56-63 (1994).
37. A. Agarwal, K.M. Davis and M. Tomozawa, J. Non-Cryst. Solids, 185, 191-198 (1995).
38. A. Agarwal and M. Tomozawa, J. Am. Ceram. Soc. 78, 827-829 (1995).
39. H. Li, A. Agarwal and M. Tomozawa, J. Am. Ceram. Soc., 78, 1393-96 (1995).