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Hardness and Low-Temperature Deformation of Silica Glass*

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Vickers diamond pyramid hardness measurements have been made on silica glass with varying thermal history using loads up to 1000 g. Hardness was independent of load and source. From interference photographs and subsequent anneal of the indentations at temperatures below T_g, it was concluded that indentation leads primarily to densification of a volume of glass in the vicinity of the indenter. A portion of the densification which is recoverable at relatively low temperatures is attributed to molecular entanglement of the glassy network due to high pressure and shear. The other portion which is not recoverable below T_g represents an approach to the final equilibrium density of the glass. Hardness of silica glass as determined by this method is thus defined as a resistance of the material to densification.

1. Introduction

The hardness of glass is of direct practical importance since it is apparently related to abrasion resistance or "scratchability". Because of its relation to "bonding" in glass, hardness has often been used as an approximate measure of strength [1, 2]. Although hardness is extensively measured and many techniques are available for its measurement, there is still no satisfactory definition as far as glass is concerned. All experimental methods for hardness determination give relative measures of low temperature (mostly room temperature) deformation which involves atom or ion migration under high local pressure and shear. It is also known that oxide glasses will undergo so-called densification under high pressure and shear conditions [3]. The objectives of the present investigation are: (i) to provide a more detailed understanding of the property known as hardness of glass, (ii) to examine the possible relationship between hardness and the pressure-induced densification of glass. In the present work, silica glass has been selected as the initial material for this investigation because it is one of the simplest oxide glasses available and its pressure-induced densification has been most widely studied. A technique has now been developed which permitted crack-free Vickers pyramid diamond indentations to be made with loads up to one kilogram [4]. Such high loads permit a much more accurate measure of hardness. After indentation, the samples were annealed and the "healing" of the defects studied at temperatures below 1200°C which is the approximate glass transition temperature for silica.

2. Experimental Procedure

2.1. Sources of Samples and Indentation

Polished fused silica discs of $\frac{1}{4}$ in. (6.25 mm) thickness were obtained from four sources to ascertain the effects of preparation history on hardness. Samples obtained from Thermal American Fused Quartz Company† were prepared by fusion of Brazilian quartz. Those from Corning Glass works‡ were prepared by flame hydrolysis of $SiCl_4$ and contained less than 1 ppm of impurities. Samples obtained from

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General Electric Company* and General Technology Corporation† were also studied, but the preparation history was not made known by the manufacturers. After these specimens were all given the identical repolishing [4], indentations were made with a Vickers Pyramid Diamond Indenter mounted on a Kentron Microhardness Tester. Indentations were made at room temperature with loads ranging from 100 to 1000 g and a loading rate of 4 mm/min was consistently used. The total loading times were kept at about 10 sec. No significant difference in the diagonal lengths of the indentations was observed for higher loading times up to 100 sec. However, shorter times resulted in wide scatter of hardness values for one set of indentations.

2.2. Photographic Technique

Photographs of indentations were taken with a Zeiss Neophot Metallograph at a magnification of 1050 ×. Several photographs of each indentation were taken, and that with the sharpest focus at the diagonal ends was used. Measurements of the walls and diagonals were made on the photograph with a cathetometer. It was possible to obtain accurate dimensions for the diagonals but not for the walls since the latter were generally not well defined. Measurements on diagonals were only read to $\pm$ 0.1 mm because of the uncertainty of precisely locating the ends.

2.3. Anneal of Indentations

Indented specimens were wrapped in platinum foil and placed into an electric furnace at the desired temperature. Approximately 5 min were required for the sample to reach the annealing temperature. Two annealing periods were studied, one for 15 min and one for 21 h. At the end of the anneal, the samples were removed from the furnace and the indentations rephotographed. Some of the samples were returned to the furnace and annealed at some higher temperature. The effects of ambient atmosphere were examined by annealing in air at one atmosphere, air at 10^{-6} torr, and dry argon at one atmosphere.

2.4. Statistical Treatment of Data

It is well known that at relatively low loads, the sizes of the indentations are only of the order of 10^{-3} cm. Secondly, it is extremely difficult to locate the ends of the diagonals exactly. The shrinkage or "healing" of indentations after annealing for a few hours may be of the order of a few per cent. Meaningful results can therefore be obtained only through a proper statistical treatment of the data. In many hardness measurements [1, 2], the two measured diagonals of each indentation are averaged *before* the standard deviation is calculated. Such treatment of data yields only an apparent standard deviation. The correct standard deviation is obtained by the use of both diagonal values rather than their average. The significance of this difference is illustrated in Appendix 1. The present experimental results were all treated by this latter more exact method.

3. Results

3.1. Hardness as a Function of Load and Source

Hardness was calculated from the equation

$$H_V = 2 \sin \theta . L/d^2 \qquad (1)$$

where H_V is the Vickers hardness number, d is the length of the diagonal, L is the applied load, and θ is the angle between opposite faces of the indenter. Typical indentation photographs are shown in fig. 1. In fig. 2, it is seen that hardness is independent of load up to 1000 g. At a load of 400 g, no variation of hardness was observed for the samples obtained from the four different sources.

3.2. Anneal of Indentations

Samples which were indented with 400 g and 1000 g loads were annealed initially for only 15 min at temperatures up to 900° C. Some such results are shown by curve A of fig. 3. No change of diagonal length was observable after anneal at temperatures up to 500°C. Some shrinkage, however, appears to have occurred after about 600° C. A much longer anneal was therefore carried out, this time for 21 h. Results for the 400 g load indentations are shown by curve B of fig. 3. These results represent the average values obtained from the same indentations on a single sample. Thus, for example, the indentations subjected to the 700° C treatment have already been annealed for 21 h at each previous lower temperature. The diagonal shrinkage after such a "cumulative" treatment was 5%. A single direct-heat treatment at 700°C for 21 h gave the identical shrinkage value. It is seen that the present shrinkage is significantly less than that

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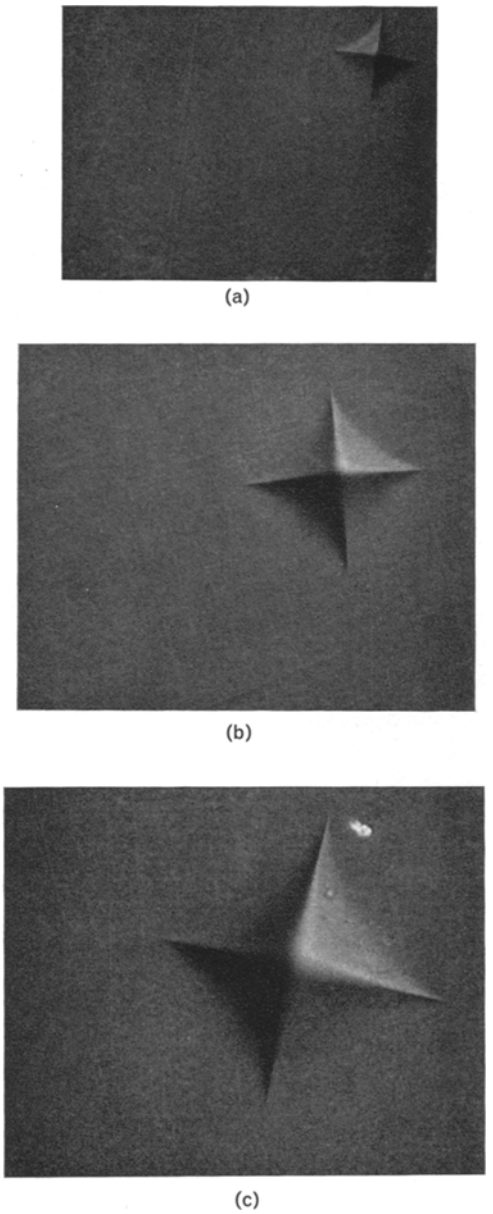

Figure 1 Typical photographs of (a) 100, (b) 400 and (c) 1000 g indentations for silica glass (×735).

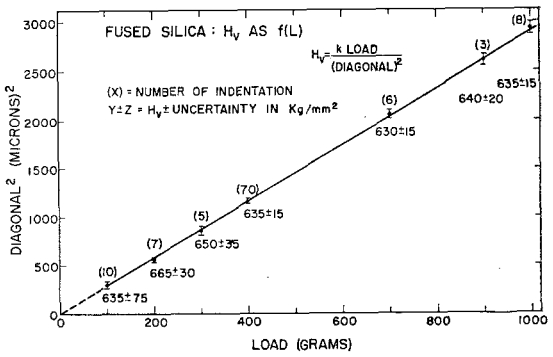

Figure 2 Relation between (diagonal)^2 and load. Figures in parenthesis represent number of indentations made at that load. Calculated hardness number with limits of uncertainty are shown in figure.

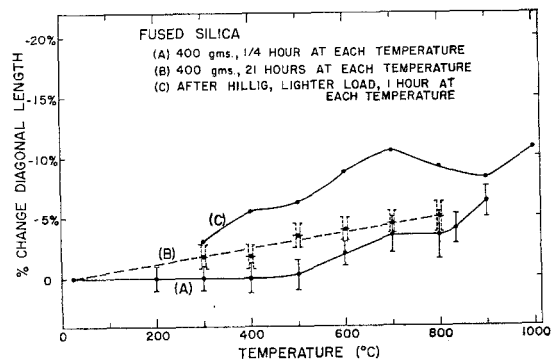

Figure 3 Variation of diagonal length of indentation with temperature for two periods of anneal.

observed by Hillig [5] as shown by curve C of fig. 3.

The effects of ambient atmosphere on anneal were studied for durations of 15 min and 21 h at 700° C. A 15 min anneal in air and pure dry argon showed no difference. Within the limits of uncertainty, the diagonal shrinkages of specimens annealed for 21 h in air and in a vacuum of 10^{-6} torr at 700° C also showed no variation. Thus, the disparity between the present results and those of Hillig are not due to differences in the ambient atmosphere. Measurement of the shrinkage of indentation walls, i.e., along a line 45° to the diagonals was difficult because of the diffuseness of the walls as seen in fig. 1. Some such results are shown in fig. 4. Despite the large uncertainty, the shrinkage along the walls is seen to be substantially greater than that along the diagonals.

3.3. Interference Photographs

For a better understanding of hardness, it is necessary to account for the volume of glass displaced in the formation of the indentation. One possible mode of displacement is by "piling-up" of material around the indentation. This possibility was checked by interference photographs made at 1500 × for a 1000 g

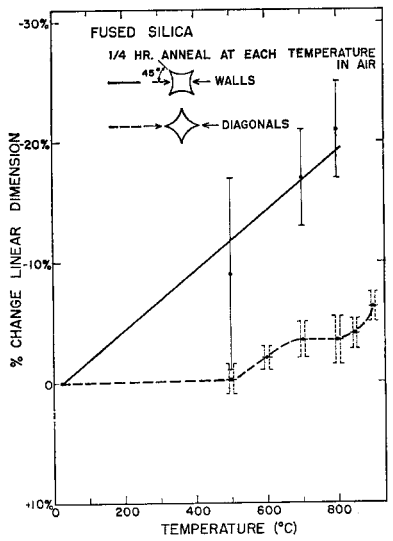

Figure 4 Comparison of the annealing behaviour of diagonals and walls of indentations.

indentation as shown in fig. 5. The interference fringes were aligned so that they approached the indentation wall perpendicularly so that any "pile-up" of material could be observed. The height, h, of an elevated region on a flat surface can be calculated from the equation:

$$h = k\lambda/2 \qquad (2)$$

where k is the ratio of linear fringe deflection to fringe spacing, and λ is the wavelength of the light source. In this work, a green filter was used with a carbon-arc source. λ is thus about 5500 Å.

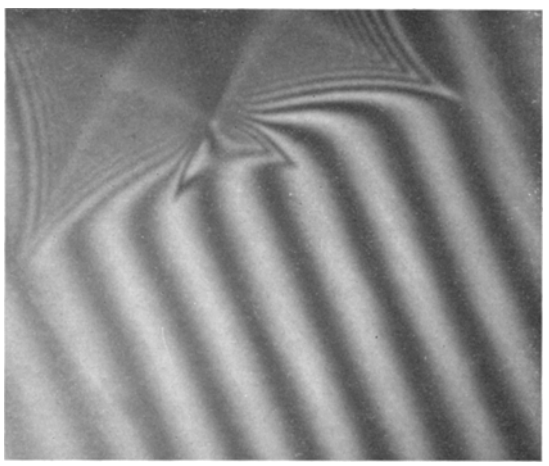

Figure 5 Typical interference photograph of a portion of a 1000 g indentation (×1500).

With the present resolution, k cannot be more than 0.1. Thus the maximum value of h if a pile-up did occur is only about 300 Å.

4. Discussion

4.1. Displacement of Glass During Indentation

The hardness indentation experiment is essentially a two-stage process. The first step involves the creation of an indentation when the indenter is pushed into the glass with an applied load. The second step involves the removal of the indenter. If an indentation such as that shown in fig. 1 is present *after* the indenter is removed, it is obvious that in addition to the recoverable elastic compression experienced by the sample, some apparent "irreversible" process has taken place. Some part of the glass in the immediate vicinity of the indenter might have been devitrified and/or material could have been actually displaced. Even under very high pressures, the minimum temperature reported at which fused silica was found to devitrify was about 500° C [6, 7]. Devitrification is thus considered unlikely. Because hardness is independent of load, from 100 to 1000 g, i.e., independent of penetration depth from 3 to 8 μm, it is likely that the displacement of glass is a bulk property rather than a surface-controlled phenomenon.

In considering material displacement, there are at least three possibilities. (i) Glass is pushed upwards on the descent of the indenter and is "piled-up" around the perimeter of the indentation. The total volume of the sample is unchanged. (ii) Glass is displaced towards a region below the indenter. There is again no decrease in the total volume of the sample. (iii) Glass is displaced towards a region below the indenter, but the total volume of the sample has now decreased by an amount approximately equivalent to the volume of the indentation *after* the removal of the indenter. In other words, some densification of the sample has occurred during indentation.

The first possibility, i.e. the piling-up of material around the perimeter of the indentation, has been reported for crystals [8]. Scratch marks on soda-lime glass also result in this form of material displacement [9]. In the present work, the penetration depth of the indenter under a 1000 g load is approximately 8 μm. On the removal of the indenter, some elastic recovery must have occurred. Thus the height of the piling-up region must be less than 8 μm but is unlikely to be less than 1 μm. The interference photo-

graph and equation 2 indicate that any piling-up cannot be in excess of 0.03 μm. This possibility is therefore considered not to be the predominant process for silica glass.

The second possibility involves a change in shape but not in the total volume of the sample, i.e. a permanent distortion arising from the compression due to the indenter and its accompanying load. The maximum stress in the parallel surface opposite to the indented surface of the sample (see Appendix 2) can be calculated approximately from

$$\sigma_{max} = L/0.6\,\pi d^2 \qquad (3)$$

where d is the thickness of the sample. For the present experiments, L_{max} is 2.2 lb (1.0 kg) and h is $\frac{1}{4}$ in. (6.25 mm). σ_{max} is therefore only 20 lb/in.^{2} (1.41 kg/cm^2). This calculation, though approximate, clearly indicates that displacement of glass leading to a permanent distortion of the bottom surface of the sample is unlikely.

Under conditions of high pressure and shear, silica glass is known to undergo densification [3]. From the hardness value of approximately 640 kg/mm^2, the *average* final pressure experienced by the glass in contact with the indenter is of the order of 10^6 lb/in.^{2} (7.1×10^4 kg/cm^2). Furthermore, the geometry of the indenter dictates a condition of shear. The third possibility of glass displacement, namely, densification, is thus to be expected. Hillig [5], for instance, has reported that the refractive index of the glass immediately surrounding the indentation is different from that of the bulk.

Marsh [10] has recently suggested that material transport during indentation occurs radially. The validity of this manner of transport can be examined if an indentation is made on an area of the glass surface which already has a scratch mark. If radial flow does occur, then after indentation, a scratch discontinuity and/or displacement as illustrated in fig. 6 should be observable. However, in fig. 7, it is seen that the scratch remains linear throughout the indented region. Material transport of fused silica during indentation has thus occurred vertically downwards rather than radially.

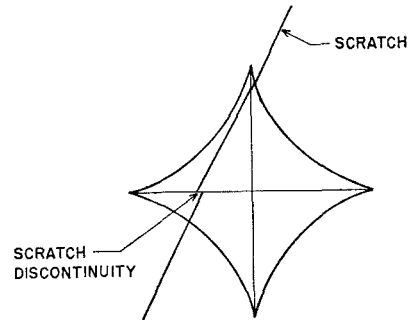

Figure 6 Hypothetical scratch profile after indentation for a radial flow mechanism.

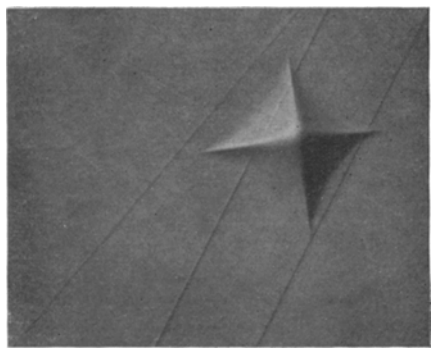

Figure 7 Photograph of an indented scratch showing no discontinuity (×735).

4.2. Mechanism of Flow

The mechanism of material transport *during* indentation is extremely difficult to study experimentally. The direct differentiation between various suggested mechanisms is therefore almost impossible. We have chosen to study the behaviour of the indentation during subsequent anneal. Some suggested mechanisms of flow are, for instance, (i) viscous flow [11], (ii) plastic flow [10], (iii) volume flow leading to "permanent densification [12], and (iv) volume flow leading to non-permanent densification [3, 6]. Both plastic flow and viscous flow are irreversible phenomena. The glass transition temperature of fused silica is about 1200° C. Thus if the indentations are annealed at temperatures below 1200° C, there should be no observable recovery. Substantial recoveries of both walls and diagonals are seen to have occurred after only 15 min at 700° C (fig. 4). Plastic flow and viscous flow are thus considered unacceptable. Further, viscous flow does not involve density changes but the presently observed indentation is apparently the result of densification of the glass.

The present results on the dependence of annealing on temperature do not permit a detailed kinetic study. However, a semi-quantitative treatment can be applied. Assuming that the recovery of the indentation is a rate process with a simple exponential dependence on

temperature, the shrinkage rate of the diagonal can be approximately described by

$$k = \mathrm{A} \exp - (E^*/RT) \qquad (4)$$

where A is a constant, and E^* is the activation energy of the process. In fig. 8, we have plotted the annealing data for the 15 min and 21 h experiments against $1/T$, assuming linear variation of shrinkage with time for these two periods. The "activation energies" evaluated from fig. 8 were 13 and 3 kcal/mole respectively. Owing to the assumptions and approximations made, no quantitative significance should be attached to these values of E^*. However, they are clearly very different from the hypothetical plot corresponding to 150 kcal/mole in fig. 8, which more truly represents viscous flow in fused silica.

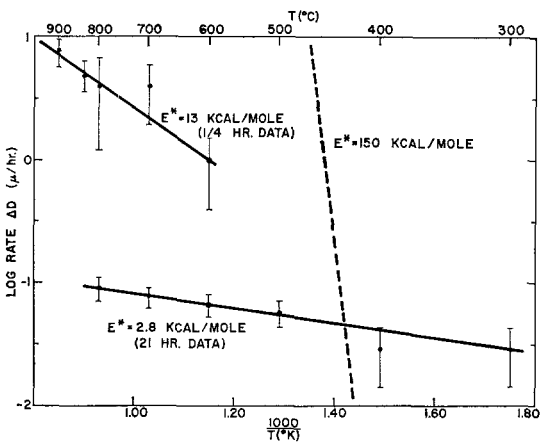

Figure 8 Relation between log shrinkage rate of diagonals for two annealing periods and $1/T$. Hypothetical slope for E^* of 150 kcal/mole is shown by dashed line.

Since recovery does take place on annealing at 700° C, the volume flow process cannot be entirely "permanent". A substantial portion of the flow process leading to "non-permanent" densification is presumably related to the network entanglement mechanism suggested for fused silica [3]. We thus suggest that in the formation of the indentation, both "permanent" and "non-permanent" densification of silica glass can occur, their ratio being primarily dependent on the geometry of the indenter, load and temperature. The difference in annealing rates observed between the walls and diagonals are probably due to the much higher pressure experienced by the glass along the edges of the indenter.

5. Conclusions

(i) Hardness of fused silica as determined by the Vickers Pyramid Indenter can be defined as the resistance of the material to densification.
(ii) A portion of the densification which occurs during indentation of fused silica occurs by a complex molecular entanglement mechanism which is reversible. This is illustrated by partial recovery at temperatures much below T_g. Another portion may be an approach to the final equilibrium density of the glass which is now irreversible.

Acknowledgements

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Appendix 1

Calculation of the standard deviation of diagonals by two methods is illustrated in table I below: Since the standard deviation is given by $S = \sqrt{(D_{av} - D_1)^2 + \ldots . (D_{av} - D_i)^2 / i}$, $S = 0.03$ cm by raw data method, and $S = 0$ by averaged data method.

TABLE I

Indentation No.	Raw data method Individual diagonals (cm)		Averaged data method Average of 2 diagonals (cm)
1	1.74	1.82	1.78
2	1.79	1.77	1.78
3	1.76	1.80	1.78
4	1.78	1.78	1.78
5	1.81	1.75	1.78
6	1.73	1.83	1.78
	10.61	10.75	10.68
Σ_D	21.36		10.68
D_{average}	1.78		1.78

Appendix 2

According to Frocht [13], on the application of a concentrated load L to a long plank of thickness d, supported by a rigid foundation, the stress distribution on the parallel surface opposite to L is concentrated on an area of diameter $2.7d$. The maximum stress $\sigma_{\max}$ in the direction of L can be estimated as follows.

At static equilibrium,

$$L = \int_{r=0}^{1.35d} \sigma_v dA \tag{1A}$$

where $dA = 2\pi r dr$, r is the horizontal distance from L, and σ_v is the stress in the vertical direction. If the stress distribution is an approximate linear function of r, then the stress at any r is given by

$$\sigma_v = (1.35d - r)\,\sigma_{\max}/1.35d \tag{2A}$$

$$L = 2\pi\,\sigma_{\max} \int_{r=0}^{1.35d} \left[\frac{(1.35d-r)}{1.35d}\right] r dr \tag{3A}$$

and $$\sigma_{\max} = L/0.6\pi\, d^2 \tag{4A}$$