

FRACTURE, PERMANENT DEFORMATION AND STRUCTURE CHANGE IN OXIDE GLASSES

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ABSTRACT

Oxide glass is known as typical brittle material, and the fracture behavior of soda-lime silicate glass, which is the most popular commercial glass, is well represented by linear fracture mechanics. However, consideration about fracture surface energy suggests that some process with energy dissipation, such as plastic deformation and/or structural change, is involved in the fracture process. Crushing a glass is found to induce a structural change. From the relaxation experiments, the main change was found to be the densification at the surface. Composition dependence of the degree of densification at crushing indicates that the glass with large free volume tends to densify easily. Indentation of glass causes both the plastic deformation and the densification. Glasses having high ratio of densification at the indentation process seem to show large densification at the crushing process. Borate glass shows an inelastic deformation behavior at the cleavage slow crack growth process. The magnitude of inelasticity depends on the stress intensity factor, but not depends on the crack velocity. Therefore, the inelastic process is the plastic deformation. Glasses that require high stress intensity factor tend to have large free volume and show a large densification at the crushing process. This suggests that some energy consumption process such as density change or deformation should be involved in the slow crack growth process of oxide glasses.

1. INTRODUCTION

Oxide glass is known as typical brittle material, which means that glass fractures without any plastic deformation. Fractography for oxide glass assists this opinion. Fracture surface of glass has sharp edge, and no trace of plastic deformation is found. In addition, lack of the periodic structure of atomic arrangement in glass is considered to make the formation and motion of dislocation impossible. Therefore, plastic deformation led by the motion of dislocation, which is called as Peierls mechanism and common in crystals, does not occur in glass. In addition, fracture behavior of soda-lime silicate glass, which is the most popular commercial glass, is well represented by linear fracture mechanics. From these facts, most of the people in materials science think it true that no plastic deformation or other structural change occur at the fracture process of glass. In other words, fracture of glass makes new glass surface but causes no change at the interior of glass. However, consideration about fracture surface energy suggests that some process with energy dissipation, such as plastic deformation and/or structural change, is involved in the fracture process.

Fracture of solids is a phenomenon that a new surface is made by mechanical stress. Fracture occurs when both of the following criteria are satisfied. One is the Griffith's energy balance criterion that the effective fracture surface energy must be equal or larger than the equilibrium surface energy. The other is the Orowan's stress criterion that the stress at the crack tip must be equal or larger than the theoretical stress of the material. For brittle material with sharp crack tip, Griffith's energy criterion is considered to determine the fracture behavior [1]. However, the fracture surface energy of oxide glasses at stable crack growth, that not includes the kinetic energy of broken glass or the energy of sound that arises at rupture, is in the range from 2 to 10 Jm⁻² [2], and is about one or two orders of magnitude larger than the static surface energy, which is about 0.2 to 0.6 Jm⁻² for many oxide glasses. Therefore, in addition to the energy to form a new surface, some energy dissipation process must be present at the fracture process of glass.

From our previous studies and studies by other researchers, stress induced phenomena related with the fracture become to be known. In this paper, studies about structure change of glass by crushing, indentation-induced densification, inelastic deformation at the cleavage fracture of borate glass are presented, and an assumption about the fracture of oxide glass is proposed.

2. STRUCTURE CHANGE OF GLASS BY CRUSHING

Crushing a glass causes the structure change in oxide glasses. Kokura *et al.* [3] reported that crushing a silica glass forms E' center, which is a kind of electronic defect with the structure of $=\text{Si}\cdot$ radical [3], and the environment at fracture affects the concentration of these defects. Another study about the inhomogeneity in refractive index of crushed glass carried out by Wada *et al.* [4] shows that crushing a glass increase the inhomogeneity, and the degree of increase depends on the glass structure. In addition, Wada *et al.* shows that annealing of the crushed glass decreases the inhomogeneity. From the viewpoint of the internal energy of glass, these phenomena can be schematically illustrated as shown in Figure 1. Crushing, which is the fracture by compressive stress, increases the energy, and relaxation occurs by annealing. The presence of relaxation means that the observed phenomena are not the plastic or viscous flow, although there is a possibility that flow exists together with the observed phenomena.

In order to clarify the phenomena, we studied the crush-induced structural change and its relaxation in silica glass [5,6]. Three properties were measured. One is the heat of solution to hydrofluoric acid, which clarifies the change in internal energy. The second is the optical scattering measurement that Wada *et al.* used, in which the optical transmittance of crushed glass powders immersed in a liquid with its refractive index equal to the average refractive index of glass indicates the measure of homogeneity. The last was electron spin resonance study to detect the E' center. Figure 2 shows the result for the relaxation of the heat of solution. Lower value means the more stable state. Heat of solution is high for as-crushed glass, and decreases in a short time less than 10hr. After that, it takes almost constant values except for the case of 1000°C. The magnitude of this decrease depends on the annealing temperature. From the data, the apparent activation energy of relaxation was calculated to be 56 kJmol^{-1} . Figure 3 shows the relaxation of the inhomogeneity in refractive index. Higher value means more the homogeneous state. Relaxation of this inhomogeneity shows a similar behavior and gives similar apparent activation energy. These observed behaviors are similar to the density relaxation of densified silica made by anvil method [7]. The apparent activation energy in this case is 42 kJmol^{-1} . These values are similar to the each other and far from the activation energy of viscous flow, which is about 500 kJmol^{-1} . Therefore, we conclude that the crushing of silica glass makes a structural change in the glass, and is the formation of densified layer at the surface. Further study indicated that the thickness of this layer is within 0.2 to $0.3 \mu\text{m}$ [8].

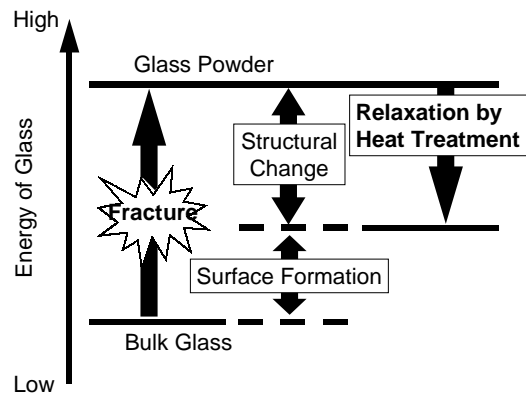


Fig.1 Schematic diagram of the energy change of glass by crushing and subsequent annealing.

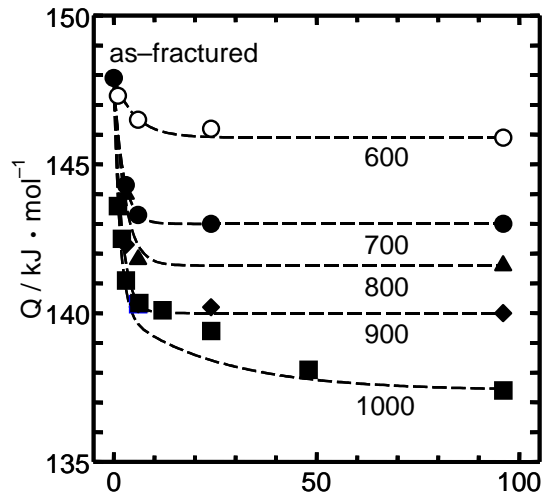


Fig.2 Change of the heat of solution to HF_{aq} of crushed silica glass as a function of the annealing time with different temperatures [6].

On the other hand, relaxation behavior of E' center shows a more rapid decrease even though the annealing temperature is as low as 400°C. In addition, decrease of the E' center by immersing the crushed sample to water indicates that the layer at which the E' center is formed is very thin. Therefore, although the mechanism of the formation of E' center may be the same as the mechanism of densification, E' center may be formed only at the highly densified thin layer, or be formed at the contact point of a crushed particle to the other particle at which shear stress should exist together with the compressive stress. From the viewpoint of internal energy, contribution of the E' center is very small. The concentration of E' center crushed with the same condition with the heat of solution measurement is 2×10^{16} spins per mole. When we assume that the formation energy of E' center is equal to the single bond strength of Si-O bond, the energy required for making E' center with this concentration is about $2 \times 10^{-5} \text{ kJmol}^{-1}$. This is much smaller than the change in heat of solution, and so the contribution to this is negligible.

Figure 4 shows the heat of solution for silica, soda-lime silicate and lead silicate glasses. It is clear that the degree of structural change, which may be densification, depends on the glass composition. It is known that the free volume of silica glass, measured by the solubility of inert gasses such as He and Ar, is very large, and that of lead silicate glass is small [9]. The behavior in Fig. 4 suggests that the increase of the free volume in glass increases the degree of densification at the crushing.

3. INDENTATION-INDUCED DEFORMATION IN GLASS

Indentation causes compressive and shear forces on the glass surface. Formation of indent in oxide glass is known as the sum of two effects, one is the plastic deformation that is common in metals and crystalline ceramics, and the other is the densification. The presence of densification makes the indentation hardness of glass low. The ratio of densification to the total inelastic deformation, i.e., (densification)/(densification + plastic deformation), can be estimated by the annealing of indented glass. Annealing causes the relaxation from densified state to normal density state, and makes the size of indent small. On the other hand, indent formed by plastic deformation does not recover by annealing [10,11]. The ratio of densification is highly dependent on the composition. Figure 5 shows the volume recovery of Knoop indent by annealing at $0.9xT_g$ for ZnO-TeO₂ glasses together with that of silica and soda-lime silicate [11]. Silica glass is easily densified, and heavy metal oxide glasses show very small

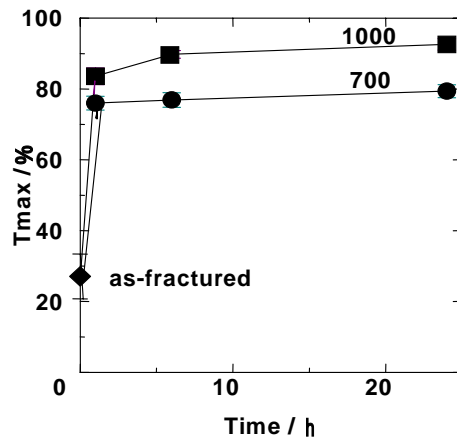


Fig.3 Homogeneity of the refractive index (Shelyubskii's maximum transmittance) of crushed silica glass as a function of the annealing time with different temperatures.

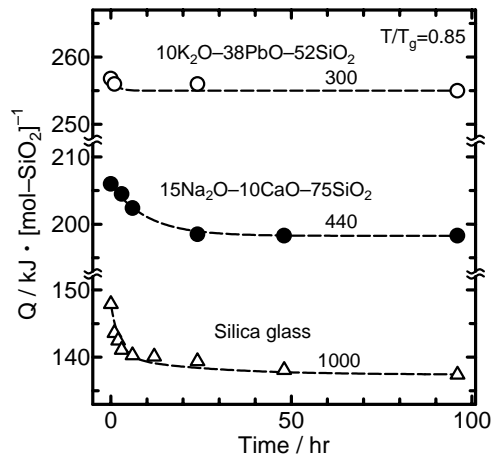


Fig.4 Heat of solution of the crushed silica, soda-lime and lead silicate glasses when annealed at a temperature of $0.85xT_g$. Vertical axis is scaled by one mole of SiO₂ in glass [6].

densification. This order is similar to the case of crushing. Therefore, although crushing causes the compressive impact stress and indentation the compressive but quasi-static stress, composition dependence seems to be the same, and governed by free volume.

In addition to the above mentioned indentation behavior, Kato *et al.* [12] demonstrated that the ratio of indentation has a relation to the easiness of crack formation, i.e., glass with high ratio of densification has high resistance to crack formation. This seems to agree with the results of crush experiment. Glass that can easily densify will form the densified layer at the surface before cracking and crushing, and glass that is hardly densify will form cracks and be crushed before surface densification occurs. The two fracture phenomena, crushing and indentation, should be correlated to each other.

4. PLASTIC DEFORMATION AT THE SLOW CRACK GROWTH OF BORATE GLASS

Crush and indentation causes the compressive stress. The remaining problem is that whether structural change and/or plastic deformation occur or not when the tension stress is applied to the glass. Borate glasses are known to have high fracture surface energy of about 10 Jm^{-2} , and large energy consumption process must be involved. We examined the loading-unloading experiment at the slow crack growth process for sodium borate glasses, and found that inelastic displacement exists in this glass system [13,14]. Figure 6 shows the relations between load and displacement, and also between inelastic displacement and displacement, of $20\text{Na}_2\text{O}\cdot 80\text{B}_2\text{O}_3$ (a) and soda-lime silicate (b) glasses at the cleavage fracture of compact tension specimen. We can see that a large inelastic deformation exists in the case of borate, but only a very small deformation exists in the case of soda-lime silicate glass.

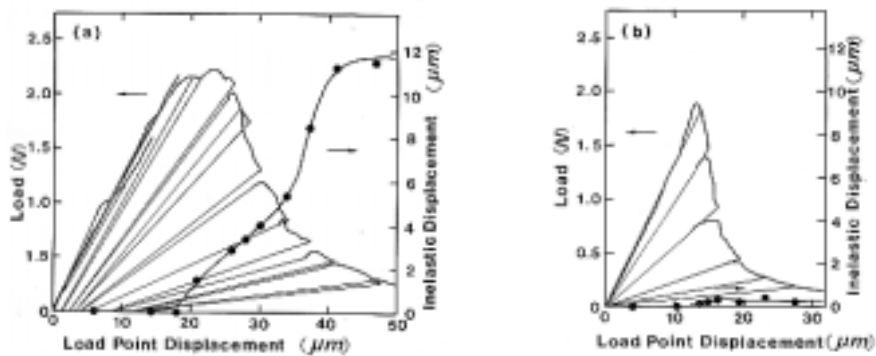


Fig. 6 Load to displacement and inelastic displacement to displacement relations on the loading-unloading experiment in dehydrated kerosene using a compact tension specimen. (a) $20\text{Na}_2\text{O}\cdot 80\text{B}_2\text{O}_3$ glass, (b) soda-lime silicate glass [14].

Inelasticity was found for the borate glass. However, it is not clear yet that the deformation is plastic, i.e., time independent, or viscous, i.e., time dependent. In addition, there is a possibility that some crystals or other reaction products is formed around the crack tip and act as pillar to prevent the recovery of

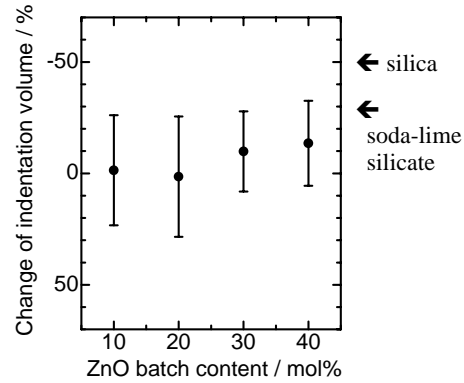


Fig.5 Volume recovery of the Knoop indent by annealing at $0.9T_g$ for $\text{ZnO}\text{-TeO}_2$ glasses. Annealing time is 2hr.

displacement. Therefore, environmental effect that changes the K_I - v (stress intensity factor to crack velocity) relation was examined. The main factor of the difference of environmental liquids should be the difference in the contamination water molecules. The data was analyzed by defining the following parameters,

$$J_I = \frac{P^2}{2} \frac{d}{dA} \left(\frac{U_e}{P} \right) = \frac{P^2}{2} \frac{d}{dA} \left(\frac{U_t - U_i}{P} \right)$$

$$I_I = \frac{P^2}{2} \frac{d}{dA} \left(\frac{U_p}{P} \right)$$

$$K_I' = \left\{ (J_I + I_I) \frac{E}{1 - \mu^2} \right\}^{1/2}$$

where P the load, A the crack area, U_e the elastic displacement, U_t the total displacement, U_i the inelastic displacement, E the Young's modulus, μ the Poisson's ratio. J_I is defined as elastic energy release rate, I_I as inelastic energy dissipation rate, and K_I' as the apparent stress intensity factor. Figure 7 shows the relation between the stress intensity factor and the magnitude of inelastic energy dissipation. It is clear that the magnitude of inelasticity depends only on the stress intensity factor, and independent from the velocity of crack growth. If the deformation were viscose, then the inelasticity would depend on the crack velocity. If the deformation were related with the growth of pillar material, then the inelasticity depends on the pillar size that would continuously be growing, and the velocity dependence would be found. The data does not agree with these possibilities, and so the inelastic deformation should be the plastic deformation.

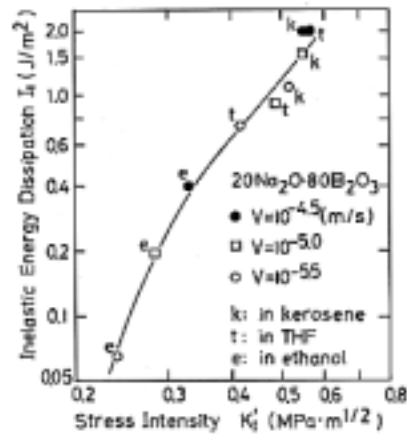


Fig.7 Dependence of inelastic energy dissipation on the stress intensity factor for $20\text{Na}_2\text{O}\cdot 80\text{B}_2\text{O}_3$ glass [14].

5. POSSIBILITY OF THE INELASTIC DEFORMATION AT THE SLOW CRACK GROWTH OF OXIDE GLASS

Direct evidence of the inelastic deformation at the slow crack process was not found yet. However, K_I - v diagram such as Figure 8 shows that the glass with large free volume tends to have high fracture toughness and high K_I values for slow crack growth, and the glass with small free volume tends to break with a weak stress. Therefore, there is a possibility that the glass that is easily densify requires the large deformation energy not only at the crushing or indentation process but also at the cleavage fracture process. This suggests that some energy consumption should be involved in the slow crack growth process of oxide glasses.

I hope this hypothesis will give a useful tool to design a strong glass composition.

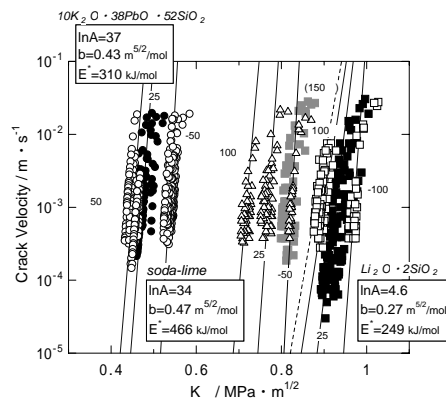


Fig.8 K_I - v diagram for some silicate glasses.

6. CONCLUSION

Crushing a glass is found to densify the surface layer of glass. Magnitude of the densification depends on the glass composition. This composition dependence seems to be equal to the ratio of densification at the indentation process. Borate glass shows a plastic deformation at the cleavage slow crack growth process. There is a possibility that other oxide glasses also have some energy consumption process at the slow crack growth.

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