Effects of Densification on Mechanical Properties of Lead Silicate Glasses

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The effects of densification on mechanical properties of \( xPbO(1-x)SiO_2 \) \((x=0.33-0.67)\) glasses were investigated. Young's modulus and hardness were increased by densification for all the lead silicate glasses. However, the fracture toughness was decreased by densification for the glasses with PbO contents larger than 40 mol%. These changes in the mechanical properties by densification were considered to be related to the disappearance of voids of an atomic scale and the irreversible structural changes affecting the network bonding character after the high pressure treatment.

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1. Introduction

Some oxide glasses such as \( \text{SiO}_2 \), \( \text{B}_2\text{O}_3 \), and \( \text{P}_2\text{O}_5 \) based glasses are known to show an increase in density even after the removal of the applied stress at room temperature. This permanent densification characteristic for glass suggests the irreversible structural change taking place in an amorphous solid at the relatively low temperatures below the glass transition, \( T_g \). Such structural change induced by densification is considered to affect directly the mechanical properties such as elastic moduli or fracture behavior, which are sensitive to the bonding and packing states of the component atoms. Only few studies have been made on the structural changes and properties of densified glasses, except those in the spectroscopic fields, since the densification treatment makes often the samples cracked and powder-like. In this work, the effect of densification on the mechanical properties was examined for lead silicate glasses, which were chosen because of the wide glass-forming region.

2. Experimental procedures

2.1 Sample preparation and high pressure treatment

The glasses having the compositions of \( xPbO(1-x)SiO_2 \) with \( x=0.33, 0.40, 0.50, \) and 0.67 were studied. Reagent grade PbO and SiO\(_2\) were mixed in an appropriate proportion and melted in a platinum crucible in an electric furnace at 1300°C for 1h. After refining, the melts were poured into a steel mold. The glass blocks obtained were annealed at an appropriate temperature lower than \( T_g \) for 3h and were cut into the cylindrical shape with 3.7mm in diameter and 7.7mm in length for high pressure treatment.

A DIA hexahedral type-hydrostatic pressure apparatus at Osaka University was used to densify the glass specimens. The specimen wrapped with a platinum foil was set together with the insulating BN in the high pressure cell made of pyrophyllite, which serves as a pressure transmitting medium. Pressures up to 6 GPa were applied to all the samples at a rate of ca. 100 MPa/min, and kept at the maximum pressure for 10 min after raising the temperature to 0.75 \( T_g \) (in K) of the glass specimen. The specimen was cooled down to room temperature by keeping the pressure constant, and then the pressure was released at room temperature. The schematic diagram showing the specimen cell assembly for densification.
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2.2 Measurements of hardness and elastic moduli

The microhardness testing was conducted by using Vickers indenter with the test load of 100 g and the indentation time of 15 s. The elastic moduli and their temperature derivatives of small densified specimens were measured by the cube resonance method. The procedure of this method was described in detail elsewhere.7) A cubic specimen with an edge length of about 2 mm was placed between the two PLZT transducers. The specimens were oscillated from one of the transducers and the resultant resonance frequencies were detected by another one. The elastic moduli were obtained from a series of resonant frequencies. Temperature dependences of elastic moduli were also measured and a slope at room temperature was used for obtaining a temperature derivative.

2.3 Measurement of fracture toughness

The Vickers indentation fracture method was employed to determine the fracture toughness of glass. The following equation given by Evans and Charles was used to calculate the fracture toughness $K_{IC}: K_{IC} = 0.027(E/H_V)^{0.4}(P/C)^{1.5}$, where $E$ is Young's modulus, $H_V$ is Vickers hardness, $P$ is the load, and $C$ is the radius of a well-developed median crack.8) A test load of 1 kgf was applied on the polishing surface in 15 s at room temperature. The tests were made at least for ten different points.

3. Results and discussion

3.1 Densification behavior

X-ray diffraction (XRD) confirmed that all the densified glass specimens remained amorphous. The composition dependence of the change in density ($\delta$) by densification treatment was shown in Fig. 2, where signs of ' and ' denote the values before and after densification treatment, respectively, so that $(\delta' - \delta'')/\delta''$ can be defined as the degree of densification. Figure 2 reveals that the degree of densification of the lead silicate glasses decreases with increasing PbO content. The decrease in densification by addition of PbO to glass indicates a difficulty in stuffing large Pb$^{2+}$ ions into the atomic scale voids existing in Si-O glass network. It also suggests that the atomic scale voids disappear with an increase of PbO content and the lead silicate glasses approach the crystalline state from the point of packing.

3.2 Hardness and elastic moduli

Figure 3 shows the composition dependence of the change in Vickers hardness by densification treatment for lead silicate glasses. The variation with PbO content below 50 mol% shown in Fig. 3 is similar to that for the behavior of density in Fig. 2. It indicates that the rate of increase in the number of bonds per unit volume by densification treatment becomes less with an increase of PbO
content. On the other hand, it is noted that the glass containing more than 50 mol% PbO exhibits the increase in the variation, which is not seen in the variation of density. It seems that this increase is due to other mechanism in addition to the increase of numbers of bonds per unit volume by densification treatment. In the previous paper, the authors reported that the composition dependence of the elastic properties changed at the composition near 50 mol% PbO. This behavior was explained in terms of the change in role of Pb²⁺ ion in glass structure from the network-modifier to the network-former when PbO content exceeded 50 mol%. This change in role of lead ions with PbO content is considered to be responsible for the increase in variation with PbO content >50 mol% as shown in Fig. 3.

The changes in Young’s modulus by densification were plotted in Fig. 4. The compositional variation in Fig. 4 is quite similar to that for hardness shown in Fig. 3. It is expected that glasses with PbO larger than 50 mol% has both the increase in bond strength of Pb-O bonding by densification and the increase of number of bonds per unit volume. Figures 3 and 4 indicate that for the glasses containing PbO<50 mol%, the contribution of bond strengthening to the increase in hardness or Young’s modulus is less than the glasses containing PbO>50 mol%. It was also found that the bonding of the Pb-O network is mainly strengthened by densification and the Si-O bonding is not strengthened. This remark was confirmed by the measurement of IR spectra as shown in Fig. 5. The Si-O stretching bands are found to shift to lower frequencies by densification in all the compositions. A quite large strengthening of the Pb-O bonding must appear in order for the increase in elastic moduli with densification to be accounted for.

Figure 6 shows the changes in temperature derivative of Young’s modulus by densification for lead silicate glasses. All the temperature derivatives of densified specimens were negative, which was the normal behavior of elasticity. It is found from Fig. 6 that densification treatments
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enhance the temperature dependence of elastic properties in the lead silicate glasses, especially in SiO$_2$-rich glasses. This would indicate that Si-O bond is more subjected to the pressure-induced change than the Pb-O bond. This is probably caused by the flexibility of Si-O-Si bond angle.$^9$ In general the softer glasses have the larger temperature dependence of elastic properties because of their shallow potentials in bonding as well as the thermal expansivity. The degree of the IR peak shift to lower frequencies for the Si-O stretching mode was maximum for the 33 mol% PbO-containing glass; 35 cm$^{-1}$ for 33 PbO mol%, 9 cm$^{-1}$ for 40 PbO mol%, 10 cm$^{-1}$ for 50 PbO mol%, 9 cm$^{-1}$ for 67 PbO mol%. This change corresponds to that of the temperature derivative of Young’s modulus for the SiO$_2$-rich glass by densification.

3.3 Fracture toughness

Figure 7 shows the variation of the change in fracture toughness by densification. Clearly, the fracture toughness of glasses containing PbO > 50 mol% decreased after densification treatment, although Young’s moduli increased as shown in Fig. 4. This indicates that the fracture energy decreases after densification for the glasses containing PbO > 50 mol%. The fracture energy $\Gamma$ can be calculated from the following relation, $K_{IC} = (2GE/(1-\nu^2))^{0.5}$ where $\nu$ is Poisson’s ratio.$^{10}$ In Fig. 8 the variation of change in fracture energy by densification were plotted for lead silicate glasses. The fracture energy can be defined as the energy required to make a new fracture surface. Providing that the applied stress is spent only in breaking chemical bonds, the fracture energy should be proportional to the number of bonds broken and their bonding strengths. But the stress applied from outside is in reality dissipated near the crack tip as the energies needed to give rise to an irregular fracture surface, crack branching, plastic deformation and the other irreversible processes. Therefore, the fracture energy should increase as these irreversible energy-absorbing processes involve in the propagation of fracture. As reported on the effects of composition on crack propagation in lead silicate glasses,$^{10}$ the energy absorption due to the plastic flow started to contribute to the fracture energy when PbO contents exceeded about 60 mol%. The densification processing is expected to make it difficult for the plastic deformation to take place near the crack tip in the densified glass, when judged from the decrease in fracture energy of the densified PbO-rich glasses shown in Fig. 8.

4. Summary

The densification treatment was conducted on the lead silicate glasses in order to elucidate the effect of densification on the mechanical properties and glass structure. The degree of densification for the lead silicate glasses was found to decrease with increasing PbO content, suggesting that the atomic scale voids disappear with an increase of PbO content. Young’s modulus and Vickers hardness were increased by the densification treatment for all the lead silicate glasses. The temperature derivatives of Young’s modulus for all the densified silicate glasses were higher than those before densification, especially remarkable in the SiO$_2$-rich region.

The fracture toughness was decreased by densification for the glasses with PbO > about 40 mol%. The fracture surface energy showed a similar compositional change to the fracture toughness. The densification treatment was expected to make it difficult for the irreversible energy-absorption process to take place near the
crack tip in the densified glass.

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