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Indentation deformation and fracture of densified silicate glass

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The Vickers hardness and Vickers indentation morphology were investigated on a predensified sodium trisilicate glass and the results were compared with those of undensified glass. By densification, the hardness increased, and well developed radial cracks appeared from four corners of the Vickers indentation, while surface flaws became less noticeable.

1. Introduction

The mechanical behaviour of silicate glasses under Vickers indenter changes greatly, depending on their intrinsic properties, peak contact load as well as environment [1–4]. Both plastic flow and densification are caused by the high stresses under the indenter. The residual stress components arising from the plastically deformed zone around the impression have been considered to be responsible for the formation of radial and lateral cracks [1, 3]. On the other hand, in borosilicate and aluminosilicate glasses, there is a large void volume compared with soda lime silica glass, where intermediate cations take up tetrahedral sites with electric compensating centres of alkali ions [5]. In such cases, densification occurs significantly, and cone cracks become their typical fracture behaviour [6–8]. The birefringence measurement by Arora *et al.* [7] indicated that less residual stress was caused around the indentations of glasses capable of densification. Also, Hagan and van der Zwaag investigated a compositional effect on several trinary glasses ranging from silica glass to commercial soda lime silica glass [4].

Under high hydrostatic pressure, an irreversible densification takes place in glasses [9]. As in silica glass [9, 10], it was considered that the densification in sodium silicate glass occurs by an intermediate structural rearrangement and the resultant decrease of void volume [11]. Recently, the mechanical properties of densified alkali borate glasses were investigated, and both Young's modulus and Knoop hardness increased with densification [12]. In such predensified glasses, less densification is thought to be caused during indentation. In this study, the morphology of Vickers indentations was observed on both undensified and densified sodium trisilicate glasses with the intention of clarifying the changes of the indentation fracture behaviour due to predensification. The results are ascribed to a decrease of indentation induced densification in comparison with plastic flow.

2. Expermiental procedure

The $Na_2O{\cdot}3SiO_2$ glass sample was prepared from reagent grade Na_2CO_3 and SiO_2. The batch composition was melted at 1400 °C for 3 h, poured into a stainless steel mould, and then annealed at the glass transition temperature for 15 min. The bulk glass thus obtained was cut into several pieces using a diamond saw. One of the pieces was ground to the shape of $\phi 3.6 \times 7.0$ mm, and placed into a heating cell for densification treatment. A hexahedra type hydrostatic pressure apparatus at Osaka University was used for preparation of the densified glass. Carbon and pyrophyllite were used as a heater and a pressure transmitting medium, respectively. After heating to 450 °C, a pressure of 5 GPa was applied at a rate of 100 MPa min^{-1} and kept for 10 min. After cooling to room temperature, the pressure was relieved. Details of the preparation method are described elsewhere [13]. During this treatment, the glass sample cleaved into discs having thicknesses of 1 mm.

A chip of the densified glass ($2 \times 2 \times 1$ mm) was mounted on a glass plate by using an adhesive agent, ground and polished with 3 μm diamond paste for Vickers indentations. The Vickers hardnesses were measured at loads of 50, 100, 200 and 500 g using a microhardness tester (M-type, Shimazu). Indentations at 1 and 5 kg were carried out by means of another hardness tester (AVK-type, Akashi). Due to the small thickness of densified glass specimens, further large load was not employed. All the indentations were performed in air, and a holding time of 15 s was used. Above 1 kg, cracks occurred. The morphologies of indentations were observed by means of a microscope (Optiphot-Pol, Nikon). In order to eliminate the

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TABLE I Densities of undensified and densified $Na_2O \cdot 3SiO_2$ glasses

	Undensified	5 GPa densified
Density, $g\,cm^{-3}$	2.437	2.624

light scattering at interior lateral cracks, the indented specimens were deposited with platinum for 2–5 min using an E102 ion sputter (Hitachi).

3. Results

The densities of undensified and densified glasses were measured by using a sink–float method, which is described elsewhere [14]. The results are shown in Table I. The density increased by about 8% after densification.

The change of Vickers hardness is shown in Fig. 1 as a function of load. Clearly, the hardness has been increased by the densification, as reported previously for borate glasses [12]. At the load of 500 g, it changed from 3.7 to 4.8 GPa. As reported previously in some materials [15–17], an indentation size effect (ISE) appears in both glasses, where the hardness decreases with increasing applied load. An environmental effect was proposed to interpret such a load dependence [15, 17]. While, Becher [18] reported that a surface hardened layer could be caused by machining. As both the glasses were polished prior to the indentation measurements, it is difficult to attribute the ISE to the intrinsic properties of the glasses.

The morphologies of Vickers indentations are shown in Figs 2 and 3 for undensified and densified glasses, respectively. At 1 kg, the densified glass manifested four straight cracks from the corners. In the case of undensified glass, however, the cracks appeared from irregular locations. At 5 kg, no well developed cracks could be observed for either of the two glasses.

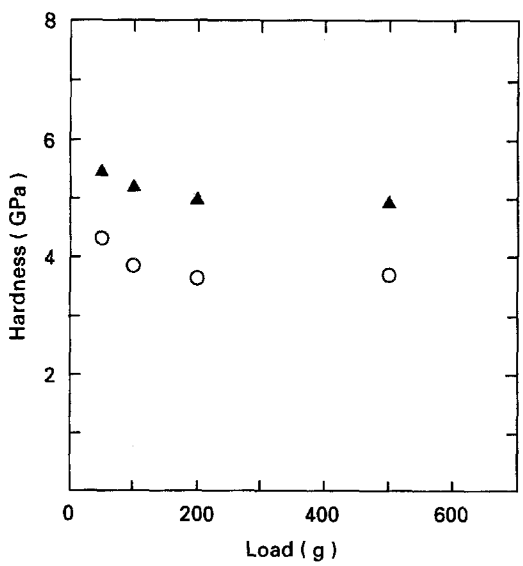

Figure 1 Vickers hardnesses as a function of load. (▲) densified glass, (○) undensified glass.

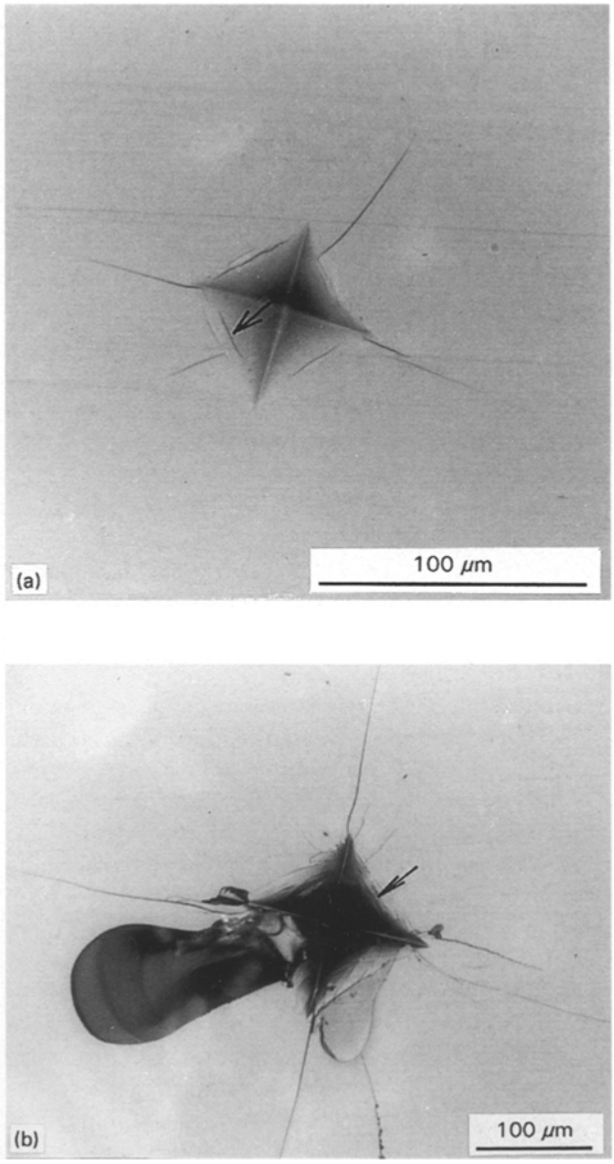

Figure 2 Photographs of indented surface of undensified $Na_2O \cdot 3SiO_2$ glass: (a) 1 kg, (b) 5 kg. The surface flaws indicated by an arrow appear within the surface of impressions or at edges.

To clarify the characteristics of the present cracks, sections of indentions parallel to the surface were observed with grinding of the surface layer. The results are shown in Fig. 4. From the traces of the cracks, they are inferred to be radial cracks, which are surface localized [1, 19]. With further grinding, these crack traces disappeared and then the impressions disappeared. Therefore, these radial cracks are not deeper than the impressions, as previously reported for soda lime silica glass [1].

In Fig. 2, another noticeable feature is the surface flaws at and outside the indentations, which are indicated by arrows. They could also be noticed in the densified glass at 5 kg (Fig. 3). But, no surface flaws could be observed at loads lower than 1 kg nor on the deeper area of the 5 kg indentations.

4. Discussion

Many authors have examined the formation of radial cracks [1, 2, 7, 19, 20]. They are thought to be caused

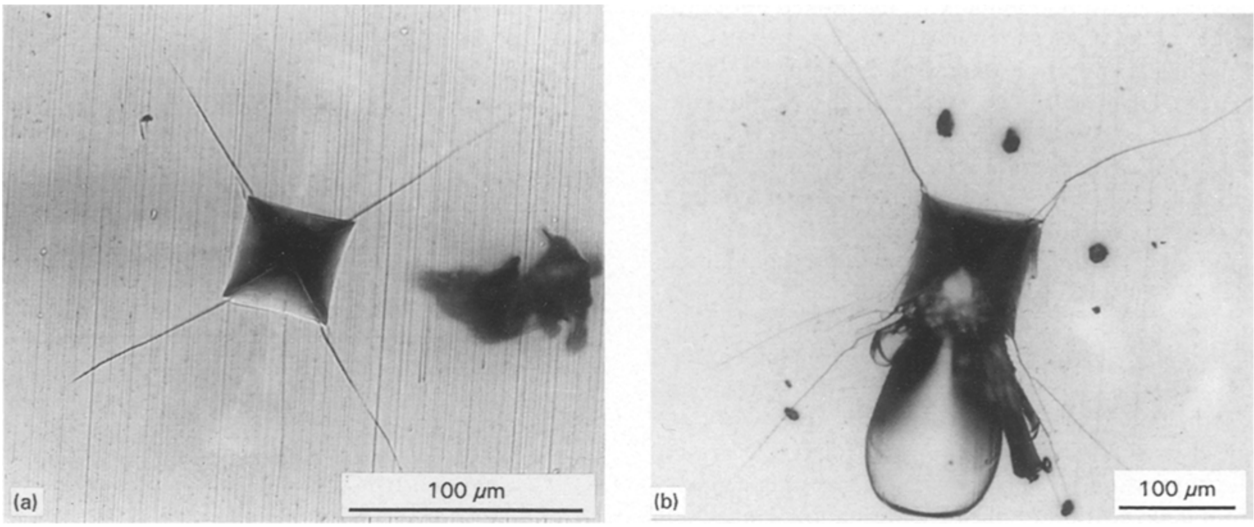

Figure 3 Photographs of indented surface of 5 GPa densified $Na_2O \cdot 3SiO_2$ glass: (a) 1 kg, (b) 5 kg.

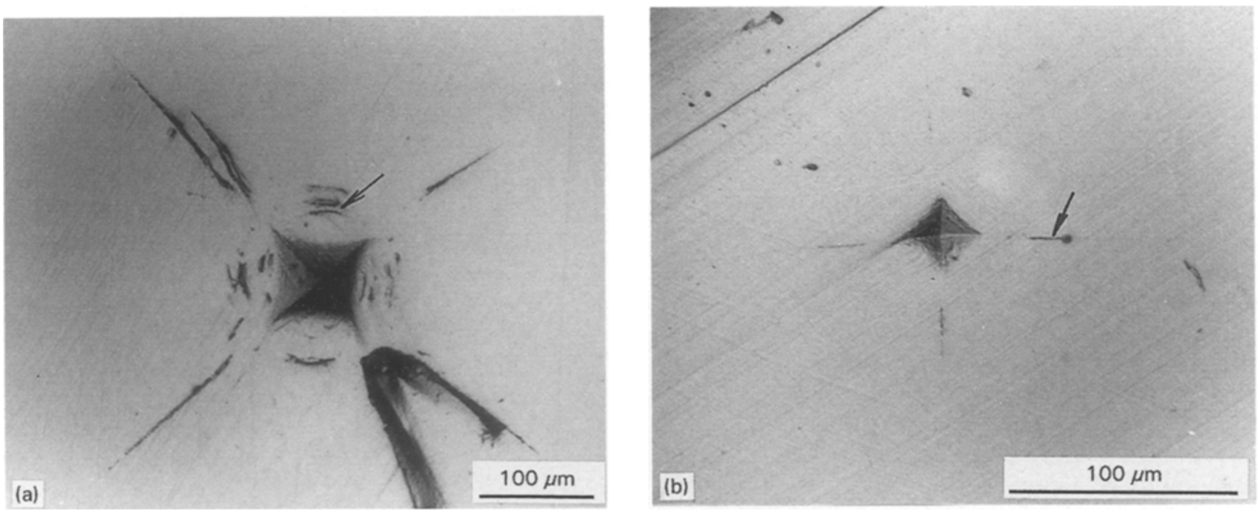

Figure 4 Photographs of the sections of the indentation parallel to surface. Their morphologies were observed by grinding of the surface layer: (a) undensified glass and a load of 5 kg, (b) densified glass and a load of 1 kg. The traces of radial cracks indicated by an arrow in (b) can be seen in both photographs. The ring faults in (a) are shown by an arrow.

by the residual stress due to the plastically deformed zone, and Lawn *et al.* [3] used a material parameter, H/E, as a measure of the driving force. For the effect of densification, especially in anomalous glasses, Cook and Pharr [1] modified this parameter by a factor of f, which changes from 0 to 1. From the fact that radial cracks become noticeable in densified glass, it can be inferred that the residual stress has been increased by predensification. Namely, the densification is relatively depressed in the two processes, as expected. However, at 5 kg, radial cracks occur at irregular locations compared with those at 1 kg. Lawn *et al.* [3] investigated the initiation mechanism of radial cracks, and proposed that they may grow from surface faults present in the impression. Therefore, the crack morphology of 5 kg may be ascribed to the surface flaws formed.

In Fig. 4, the ring faults around the impression of undensified glass are considered to continue up to the surface, leaving surface flaws. By further grinding, they were found to be shallower then the impression. Similar surface faults have been reported on silica glass and soda lime silica glass [2, 6, 7]. In soda lime silica glass, Lawn *et al.* [2] concluded that the flaws appeared at the impression due to an extension of the shear slip lines under the indenter. While, in silica glass, little shear slip lines appeared, a densified zone manifested [4, 21]. According to previous reports [6, 7, 19], they are generated at or near the indentation edges due to tensile radial stresses during the loading process. Furthermore, Arora *et al.* [7] attributed cone cracks to the growth of flaws with increasing load. The present flaws seem to resemble those of silica glass. In Fig. 2a, these flaws appeared at the edges of the impression, in agreement with this initiation mechanism. With increasing load, new cracks are initiated and absorbed into the impression. Less flaws appeared in the densified glass. This is very understandable from the change in volume consuming processes due to predensification. Plastic processes become relatively dominant as mentioned above; the origin of the flaws arising from the elastic Boussinesq stress field is relatively depressed due to the formation of a plastically deformed zone [1, 3, 22]. Furthermore, the indenter geometry can cause a distribution in the stress field, which can be seen in polarized light micrographs [7]. In Fig. 4a, no ring faults appeared at the corners of the impression. This implies that the densification effect may be relatively small at the corners. This may also be related to the fact that radial cracks always tend to grow in diagonal directions.

Peter [21] reported the difference in indentation morphology between a binary soda silica glass and a soda lime silica glass. With the introduction of CaO, shear lines under indentation and piling-up around the impression become apparent, suggesting a change from densification to plastic deformation. Hagan and van der Zwaag [4] investigated the effect of modifier cations on the indentations, where both CaO and Na_2O were introduced. The increase of these cations induced a change in the mechanical processes under indenters from silica glass to commercial soda lime silica glass, but the slip lines were apparent in their Vickers indentations. Therefore, CaO may take an important role in increasing the packing density, and the binary soda silica glasses can be classified as "anomalous glasses". Although increased modifier cations are considered to increase plastic characteristics of the deformation under high pressure [4, 23], there may be a large void volume in a binary alkali silicate glass from the densification under high hydrostatic pressures [11]. The open structure should be responsible for the densification under an indenter [6, 7, 24, 25]. Even in normal soda lime glass, densification occurs under high pressures [26], and this is expected to occur during indentation as well. As a result, the indentation technique based on an idealized deformed zone tends to give higher fracture toughnesses than those from conventional methods [27, 28]. Cook and Lawn [29] have proposed a modified indentation technique, where the direct evaluation of residual stress is eliminated. Clearly, the present results further clarify the effect of densification in indentation.

5. Conclusions

By densification, the hardness of $Na_2O \cdot 3SiO_2$ glass increased, and the indentation morphology changed greatly. The surface flaws at indentations were depressed and clear radial cracks appeared. The results can be explained from the relative decrease of densification under the indenter. In densified glass, shear plastic flow largely occurs; consequently, well developed radial cracks are generated. On the other hand, in undensified glass, the densification takes place greatly, and more surface flaws appear on the contact surface.

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References

1. R. F. COOK and G. M. PHARR, *J. Amer. Ceram. Soc.* **73** (1990) 787.
2. B. R. LAWN, T. P. DABBS and C. J. FAIRBANKS, *J. Mater. Sci.* **18** (1983) 2785.
3. B. R. LAWN, A. G. EVANS and D. B. MARSHALL, *J. Amer. Ceram. Soc.* **63** (1980) 574.
4. J. T. HAGAN and S. VAN DER ZWAAG, *J. Non-Cryst. Solids* **64** (1984) 249.
5. D. E. DAY and G. E. RINDONE, *J. Amer. Ceram. Soc.* **45** (1962) 489.
6. J. T. HAGAN, *J. Mater. Sci.* **14** (1979) 462.
7. A. ARORA, D. B. MARSHALL, B. R. LAWN and M. V. SWAIN, *J. Non-Cryst. Solids* **31** (1979) 415.
8. R. TANDON, D. J. GREEN and R. F. COOK, *J. Amer. Ceram. Soc.* **73** (1990) 2619.
9. P. W. BRIDGMAN and I. SIMON, *J. Appl. Phys.* **24** (1953) 405.
10. S. SUSMAN, K. J. VOLIN, R. C. LIEBERMANN, G. D. GWANMESIA and Y. WANG, *Phys. Chem. Glasses* **31** (1990) 144.
11. Z. ZHANG, N. SOGA and K. HIRAO, *J. Non-Cryst. Solids* **135** (1991) 55.
12. K. HIRAO, Z. ZHANG, H. MORITA and N. SOGA, *J. Soc. Mater. Sci. Jpn* **40** (1991) 400.
13. N. SOGA, K. HIRAO, M. YOSHIMOTO and H. YAMAMOTO, *J. Appl. Phys.* **63** (1988) 4451.
14. T. HANADA, N. SOGA and M. OHKAWA, *Adv. Ceram.* **24** (1988) 319.
15. R. E. HANNEMAN and J. H. WESTBROOK, *Phil. Mag.* **18** (1968) 73.
16. P. J. BURNETT and T. F. PAGE, *J. Mater. Sci.* **19** (1984) 845.
17. K. HIRAO and M. TOMOZAWA, *J. Amer. Ceram. Soc.* **70** (1987) 497.
18. P. F. BECHER, *ibid.* **57** (1972) 107.
19. J. T. HAGAN and M. V. SWAIN, *J. Phys. D: Appl. Phys.* **11** (1978) 2091.
20. B. R. LAWN and M. V. SWAIN, *J. Mater. Sci.* **10** (1975) 113.
21. K. W. PETER, *J. Non-Cryst. Solids* **5** (1970) 103.
22. E. H. YOFFE, *Phil. Mag. A* **46** (1982) 617.
23. F. M. ERNSBERGER, in "Glass: science and technology", Vol. 5, edited by D. R. Uhlmann and N. J. Kreidl (Academic Press, New York, 1980) pp. 1–19.
24. J. E. NEELY and J. D. MACKENZIE, *J. Mater. Sci.* **3** (1968) 603.
25. F. M. ERNSBERGER, *J. Amer. Ceram. Soc.* **51** (1968) 545.
26. H. M. COHEN and R. ROY, *ibid.* **44** (1961) 523.
27. G. R. ANTISIS, P. CHANTIKUL, B. R. LAWN and D. B. MARSHALL, *ibid.* **64** (1981) 533.
28. P. CHANTIKUL, G. R. ANTISIS, B. R. LAWN and D. B. MARSHALL, *ibid.* **64** (1981) 539.
29. R. F. COOK and B. R. LAWN, *ibid.* **66** (1983) C200.

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