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Effects of Prior Neutron Irradiation on Stress Build-up in Glass Caused by Ultra-Violet Light

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Ultra-violet light causes compaction of borate and borosilicate glasses, building up stresses in the irradiated surface layers. Assumed mechanisms of the stress build-up are briefly reviewed; they are based on the double bond character of the network of the glasses and the compaction processes start with photoexcitation, charge transfer or photoionisation of ⋗B–O or ⋗B–O⁻ structural units of the glasses.

The effects of prior neutron irradiation on the kinetics of the stress build-up and thermal release of the stress are examined. Prior neutron irradiation gives distinct changes in the kinetics of the stress build-up even at very low doses such as 10^7 neutrons/cm^2, causing an additive stress which appears and saturates within the early stage of ultra-violet irradiation. The effects of prior neutron irradiation disappear by successive heating at temperatures lower than 300° C. The stress enhanced by prior neutron irradiation is also thermally released by heating in the same temperature range. The threshold wavelength for the stress in neutron irradiated glass is similar to that in glasses not neutron irradiated.

The π-bond character of the glass network seems to make the kinetics of the stress build-up sensitive to neutron irradiation even at low doses. Prior neutron irradiation forms a region in the glass network in which the stress build-up by ultra-violet light is facilitated, while elsewhere the kinetics of the stress build-up remain unchanged.

1. Introduction

Stress build-up was found in the surface layer of a borosilicate glass bulb used as the protection tube of a high power mercury discharge lamp [1, 2]. The lamp was used in a photochemical reaction vessel and the inner surface of the bulb was irradiated by intense ultra-violet light emitted from a discharge tube made of transparent fused silica glass. Experiments indicated that the stress is caused by contraction of the glass structure (density increase) in the irradiated surface layer and that the extent of the stress is related to glass composition and to minor additions to the glass. Photoelastic observation of the cross-section of the glass bulb shows a high tensile stress in the thin surface layer (fig. 1).

This paper gives, (i) a brief description of the assumed mechanisms of the stress build-up, (ii) investigations of the effects of prior neutron irradiation on the kinetics of the stress build-up by ultra-violet light, and (iii) discussions on the relation between the effects of prior neutron irradiation, the disordered structure of neutron irradiated glass and the kinetics and the mechanisms of the stress build-up.

2. Assumed Mechanisms of the Stress Build-up by Ultra-Violet Light

It has been found in previous work that [1-8]:

(i) The stress build-up by ultra-violet light is observed only in glasses containing both boron and alkali oxides. Very small amounts of alkali oxides are sufficient for the stress build-up.

(ii) Minor additions to the glass, namely, various kinds of metal oxides, chalcogenides and halides have strong effects on the value of the stress.

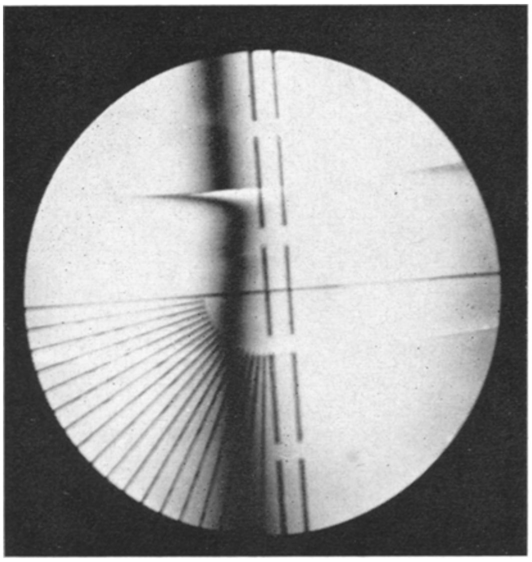

Figure 1 Photoelastic observation with Babinet compensator of a cross-section of a glass tube showing high tensile stress at the inner surface.

(iii) The conditions of glass melting (oxidising, neutral or reducing atmosphere) also affect the value of the stress.

These findings suggested that the stress build-up is of a structure-sensitive nature.

Chemical bonds in borate glass have the following peculiarities: The three-co-ordinated boron ion has three sp^2 hybrid σ-orbitals and a vacant p-orbital. The latter forms additional π-bonds with neighbouring oxygen ions (fig. 2), giving a double bond character to B–O or B–O^- bonds. This enables the bonds to twist, elongate or to form new bonds under the excitation or ionisation effects of ultra-violet light.

The possible mechanisms of the stress build-up, that is the structural change of the glass were assumed to be as follows [6]:

(i) Change of bond angle and bond length in excited B–O–B or B–O^- units.

(ii) Formation of a new bond between a non-bridging oxygen ion in a BO_3 group caused by elongation of the excited B–O^- unit. This results in the conversion of a BO_3 triangle to a BO_4 tetrahedron (fig. 3a).

(iii) Formation of a new bond and conversion of a BO_3 triangle into a BO_4 tetrahedron which is initiated by electron transfer from an oxygen ion to a boron ion in a B–O^- unit (fig. 3b).

(iv) Formation of a new bond and conversion of a triangle into a tetrahedron which is initiated by photoionisation of a non-bridging oxygen ion in a B–O^- unit (fig. 3c).

All these processes are based on the excitation

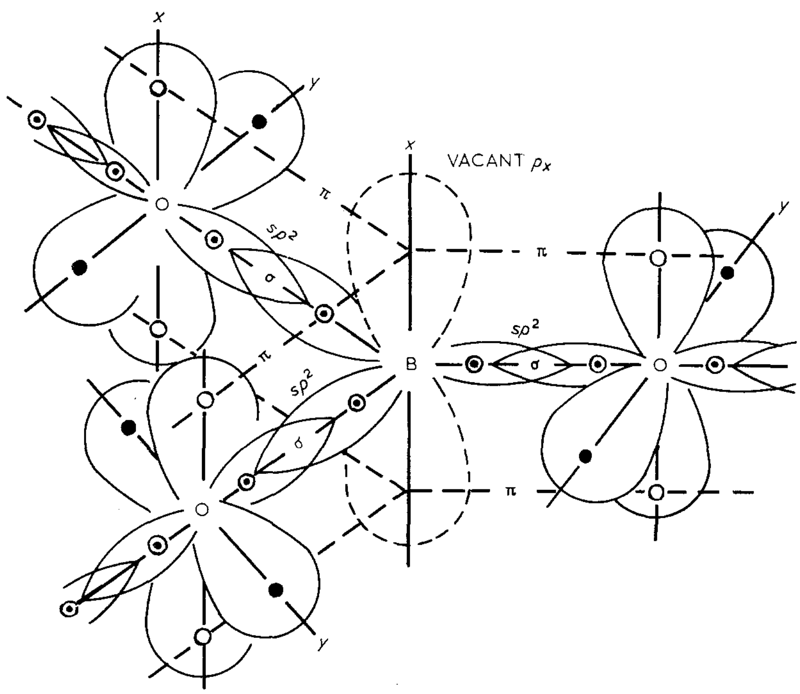

Figure 2 Electronic configuration and chemical bonds in the network of borate glass.

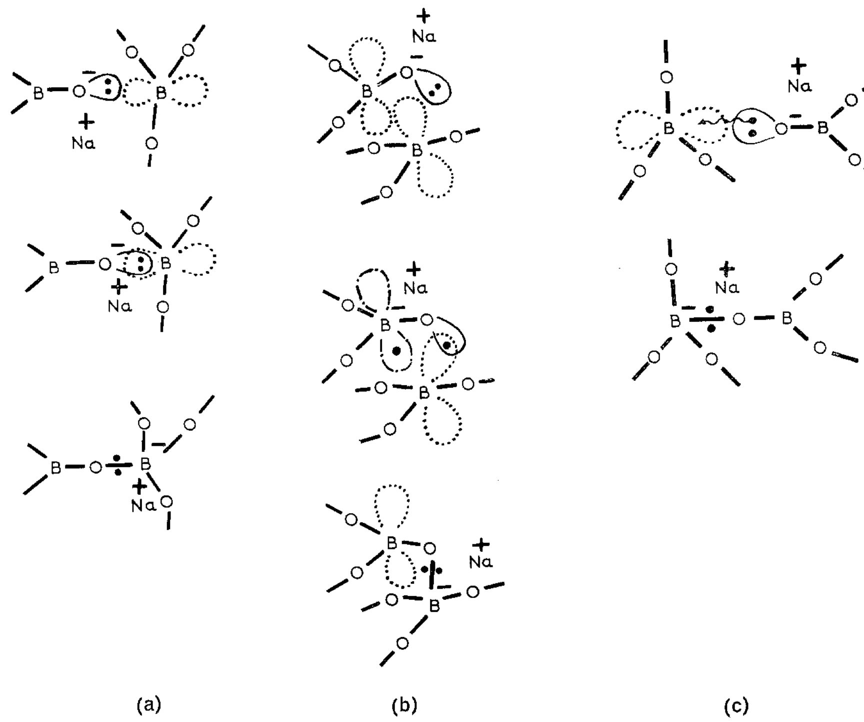

Figure 3 Processes of the structural change of borate glass by ultra-violet light caused by (a) excitation and elongation of B–O⁻ unit; (b) charge transfer in B–O⁻ unit; (c) photoionisation of non-bridging oxygen. —•—•— : orbital containing unpaired electron; - - - - : vacant *p*-orbital of boron; ——— : lone pair of oxygens; ●: electron.

or ionisation of chemical bonds in borate glass by ultra-violet light and are compatible with the structure-sensitive character of the stress build-up. Prior neutron irradiation would be expected to affect the structure of borate or borosilicate glasses by thermal spikes, knock-on or the nuclear reaction

$$_5B^{10} + {_0n^1} \rightarrow {_3Li^7} + {_2He^4} + 2.5\ \text{MeV}$$

and cause colour centre formation to occur. The effects of prior neutron irradiation on the kinetics of the stress build-up by ultra-violet irradiation were investigated.

3. Experimental Method

The glass investigated was a commercial borosilicate glass (composition in wt %: SiO_2: 80, B_2O_3: 13, Na_2O: 4, K_2O: 1, Al_2O_3: 2). Prisms of the glass 20 × 20 × 5 mm³ with polished surfaces were formed and were subjected to neutron irradiation in a nuclear reactor. The thermal output of the reactor was varied from 5 to 100 W and the irradiation time was from 10 sec to 3 h respectively, depending upon the value of dose planned. Some prisms were left unirradiated with neutron flux as reference samples. All the prisms were then subjected to ultra-violet irradiation. The light source of ultra-violet light was a 400 W mercury discharge lamp made of fused glass silica (17 mm in diameter and 150 mm in length). The prisms were cooled by a flow of air during the ultra-violet irradiation.

The stresses at the irradiated surface layers of the prisms were measured photoelastically using a Toshiba precision strain meter fitted with a Babinet compensator. Some of the stressed samples were then heated in an electric furnace at the rate of 5° C/min in order to examine the thermal release process. Additionally, the threshold energy for the stress build-up in glass was determined by inserting various glass filters between the light source and sample prisms.

4. Experimental Results

Sample prisms irradiated with a neutron flux ranging from 10^7 to 10^{15} neutrons/cm² were then subjected to ultra-violet light. Time vs. stress relations of the neutron irradiated glass are very different from that of the reference glass (fig. 4). The kinetics of the neutron irradiated glasses, however, are similar to each other except for

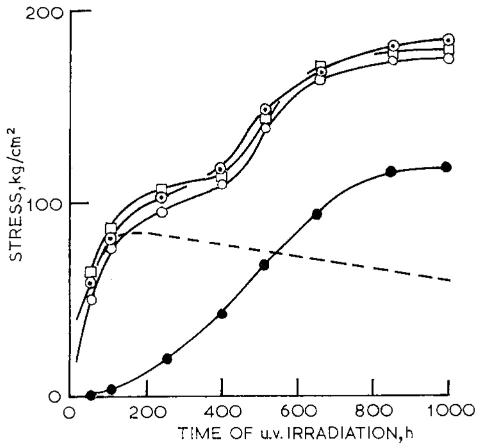

Figure 4 Kinetics of the stress build-up in the reference (not neutron irradiated) and in neutron irradiated glasses. The distance (l) between the axis of the discharge lamp and the sample surface was 20 mm. Values of the prior neutron irradiation: ○—○—○: 10^7 n/cm²; ⊙—⊙—⊙: 10^{10} n/cm²; □—□—□: 5.4×10^{14} n/cm²; ●—●—●: not irradiated; - - - -: difference (⊙ − ●).

the slightly lower value of the stress in the glass which received the lower dose.

Samples irradiated with the neutron flux were subjected to ultra-violet irradiation at various distances (l) between the axis of the light source and the irradiated surfaces. The relationship between the stress observed after 1000 h of ultra-violet irradiation and l is shown in fig. 5.

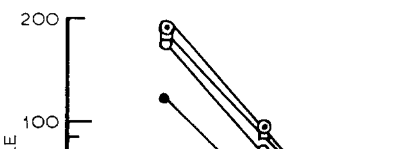

Figure 5 Relation between the distance l and the stress in the reference and neutron irradiated glasses after 1000 h of ultra-violet irradiation. Value of prior neutron irradiation: ○—○—○: 10^7 n/cm²; ⊙—⊙—⊙: 10^{10} n/cm²; □—□—□: 5.4×10^{14} n/cm²; ●—●—●: not irradiated.

Samples irradiated with a neutron flux of 5.4×10^{14} neutrons/cm² were first heat-treated at 200, 240, and 300° C, respectively, and then subjected to ultra-violet light. The kinetics of the stress build-up in these samples are shown in figs. 6, 7 and 8 respectively. The effect of prior neutron irradiation completely vanishes by heating at 300° C for less than 10 min. The kinetics of glasses treated at 240° C show a gradual conversion from that of neutron irradiated glass to that of the reference glass with increasing time of heat-treatment.

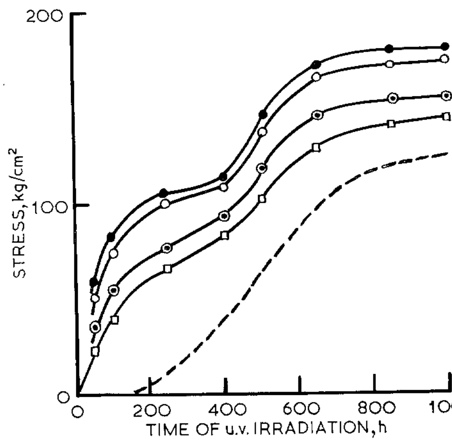

Figure 6 Kinetics of the stress build-up by ultra-violet light in glasses subjected to prior neutron irradiation of 5.4×10^{14} neutrons/cm² and successive heating at 200° C for various times (l = 20 mm). ○—○—○: 10 min; ⊙—⊙—⊙: 70 min; □—□—□: 150 min; ●—●—●: not heated; - - - -: reference curve.

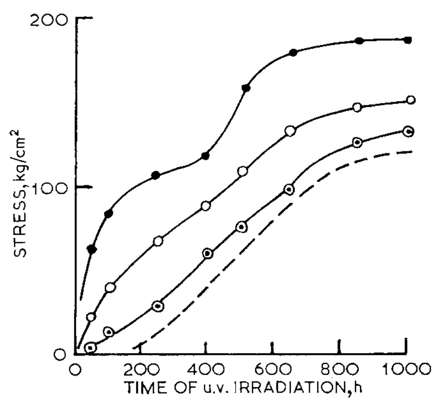

Figure 7 Kinetics of the stress build-up in glasses subjected to prior neutron irradiation of 5.4×10^{14} neutrons/cm² and successive heating at 240° C for various times (l = 20 mm). ○—○—○: 30 min; ⊙—⊙—⊙: 120 min; ●—●—●: not heated; - - -: reference curve.

Thermal release curves of the stresses are shown in fig. 9. In glasses subjected to prior neutron irradiation and subsequent ultra-violet irradiation of 1000 h, two steps of thermal release are clearly seen at about 200 and 400° C.

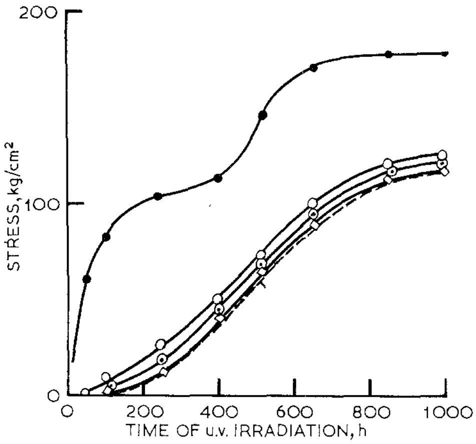

Figure 8 Kinetics of the stress build-up in glasses subjected to prior neutron irradiation of 5.4×10^{14} neutrons/cm^2 and successive heating at 300° C for various times (l = 20 mm). ○—○—○: 10 min; ⊙—⊙—⊙: 70 min; □—□—□: 150 min; ●—●—●: not heated; - - -: reference curve.

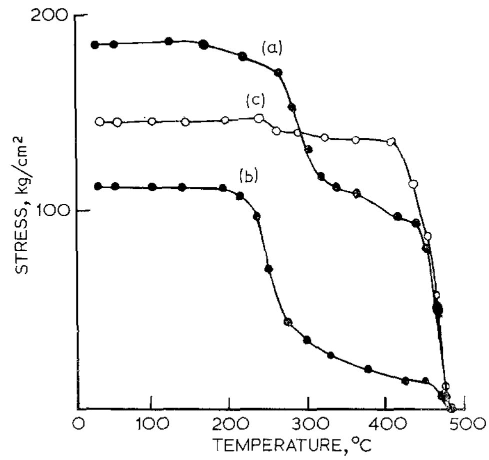

Figure 9 Thermal release of the stresses observed in glasses (a) subjected to prior neutron irradiation of 5.4×10^{14} and subsequent ultra-violet irradiation for 1000 h; (b) subjected to prior neutron irradiation of 5.4×10^{14} and subsequent ultra-violet irradiation for 300 h; (c) subjected to intensive ultra-violet light as the protection bulb of the mercury lamp (without prior neutron irradiation).

In glass subjected to prior neutron irradiation and successive ultra-violet irradiation of 300 h, most of the stress is released in the temperature range lower than 300° C. The thermal release curve of the stress in glass irradiated with ultra-violet light without prior irradiation with neutron flux is considerably different from that of the stress in glass subjected to prior neutron irradiation, as seen in the figure.

The transmission curves in the ultra-violet regions of the glass filters used to examine the threshold wavelength, that is, the threshold energy for the stress build-up are shown in fig. 10. No stress was observed after 1000 h of ultra-violet irradiation when no. 1 filter was inserted. By inserting the other filters, however, stresses were observed and the values of the stresses were found to have a linear relationship with the transmission of the filters at 220 mμ, as shown in fig. 11. Therefore, the threshold energy for the stress build-up is 220 mμ, that is, 5.7 eV.

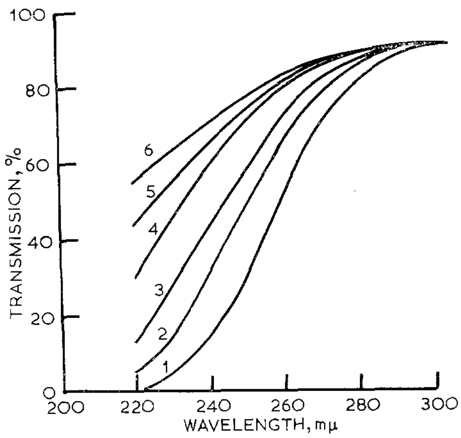

Figure 10 Transmission curves of glass filters for studying the threshold energy for the stress build-up. Numbers on the curves show the filter number.

5. Discussion and Concluding Remarks

From the above experimental results, it can be concluded that the stress in glass subjected to prior neutron irradiation is built up during ultra-violet irradiation by the superposition of two mechanisms; one is similar to that in the reference glass and the other is believed to be enhanced by prior neutron irradiation. The latter builds up and saturates quickly in less than 200 h and is released by heating at relatively low temperature, i.e. lower than 300° C. The en-

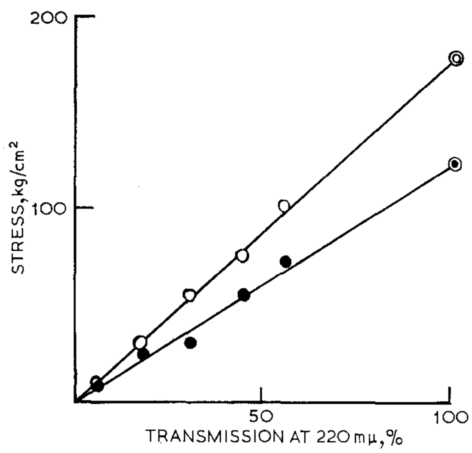

Figure 11 Relations between the transmission of inserted filters at 220 mμ and the stress observed in the reference and neutron irradiated glasses. ●—●—○: reference glass; ○—○—◎ : neutron irradiated glass.

hancement of the stress build-up by prior neutron irradiation is clearly observed even at doses which are very low (10^7 neutrons/cm^2) compared to those in most cases of radiation damage in solids, which have been reported to be bigger than 10^{16} neutrons/cm^2.

The fact that the stress value is proportional to the intensity of ultra-violet light (the intensity of ultra-violet light is inversely proportional to *l*, as shown in fig. 5) suggests that the process of the stress build-up in both the reference and neutron irradiated glasses is a one-photon process. The threshold energy for the stress build-up seems to be similar in both glasses, indicating that the basic mechanisms of the stress build-up do not differ from each other in the reference and the neutron irradiated glasses.

The enhancement effect of prior neutron irradiation is thermally released at temperatures lower than 300° C as shown in figs. 6, 7 and 8. In the same temperature range the stress caused in glass subjected to prior neutron irradiation is thermally released. This suggests that close relations exist amongst the disordered structure of neutron irradiated glass and the enhancement effects by neutron irradiation and the mechanism of the enhanced stress build-up. Thermal disintegration of the disordered configuration of the glass structure simultaneously causes disintegration of the enhanced compacted structure.

The disordered structure of neutron irradiated glass is caused by a knock-on, nuclear reaction of B^{10} and a thermal spike effect. The fraction of the disordered site is expected to be small; for example, at the dose of 10^7 neutrons/cm^2 only 10^{-14}, and at the dose of 10^{13} neutrons/cm^2 only 10^{-8} boron atoms in the surface layer react with neutrons. The effects of the disordered configurations are, however, propagated along the network of glass through π-bonds, forming regions in which the stress build-up is enhanced and accelerated. This makes the kinetics of the stress build-up by ultra-violet light sensitive to prior neutron irradiation. In other regions of the glass network the kinetics of the stress build-up remain unchanged.

The separation of the effects of thermal and fast neutrons is now being studied by the authors.

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