25. Thermal Release of Stress in Glass Caused by Ultra-violet Irradiation

Stress in Glass Caused by Ultra-violet Irradiation (Part 5)

By

Kazuo ÔOKA and Toru KISHII

(Tokyo Shibaura Electric Co., Kawasaki, Japan)

Abstract

By heating pieces of borosilicate glass (SiO_2 81, B_2O_3 12, Na_2O+K_2O 4.5, Al_2O_3 2.5 wt%) with surface stress caused by ultra-violet irradiation, stress relaxation process was observed. Results were as follows:

1. By heating up with the rate of 5°C/min, stress began to be released at about 250°C, faded away perfectly at 470°C, and did not reappear on cooling.

2. By soaking at 400°C, stress faded away perfectly in 30 min. By soaking at temperatures between 250° and 360°C, stress decreased in initial periods of about 30 min, and then attained at approximately constant values. The higher the soaking temperatures were, the less were these values, which did not change distinctly after cooling.

3. The temperatures described above were considerably lower than the annealing point (about 555°C) of the glass.

From these results, it was concluded that:

1. Stress is released by several mechanisms which participate in different temperature ranges.

2. Activation energies of relaxation mechanisms are presumed to be 35 kcal/mol or smaller, and are considerably lower than that of viscous flow (about 100 kcal/mol).

3. The stress relaxation is, therefore, presumed to be a result of, for example, reformation of deformed chemical bonds (bond angles, interatomic distances and so on) and not a result of rearrangement of network forming ions.

4. The same is possibly true for mechanisms of stress build-up.

1. Introduction

Stress build-up in glass by ultra-violet irradiation was reported[1]. By heating, the stress was released at relatively low temperatures[1),2),3)]. Detailed studies on the stress relaxation process seem to make it possible to elucidate the mechanism of stress build-up. In this paper, results of experiments on the stress relaxation are described.

2. Samples and Method of Experiment

Three kinds of glass samples were examined; a protection tube of an ordinary high pressure mercury discharge lamp, and those of two kinds of high pressure mercury lamp with relatively high output in visible wavelength region. The glasses were "Terex glass" with the composition of SiO_2 81, B_2O_3 12, Na_2O 4.5, Al_2O_3 2.5 in weight % (Table 1). Stress was measured by photoelastic apparatus with Babinet compensator.

Table 1. Samples used for experiments.

Sample	A	B	C
Origin	Protection tube of an ordinary mercury lamp	Protection tube of a mercury lamp with relatively high output in visible region	Same as B
Stress at irradiated surface, kg/cm²*	159	44	91
Thickness of stressed layer, mm*	0.13	0.14	0.14

* : Slight errors were inevitable owing to experimental difficulties.

Although the measurement of stress in irradiated thin surface layer was not highly precise owing to experimental difficulties, it was sufficient for semi-quantitative observation.

3. Experimental Results

3.1 By heating up the samples A and B, at the rate of 5°C/min, stress began to be released at about 250°C, and perfectly faded away at about 475°C (Fig. 1). During cooling, stress did not reappear.

3.2 By heating the sample A according to the schedule of 270°C, 60 min-300°C, 60 min-350°C, 80 min-400°C, 20 min, stress diminished stepwise with the increase in soaking temperature (Fig. 2).

3.3 Pieces of the sample C were subjected to heating (5°C/min)-cooling (2°C/min) cycles. The maximum temperatures in each run were 320°, 360°, 375° and 400°C respectively. Change of stress during these cycles is shown in Fig. 3.

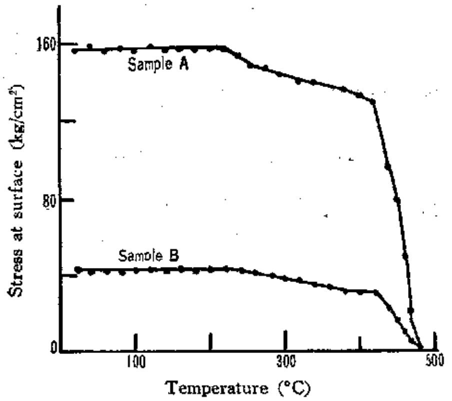

Fig. 1. Change of stress during heating-up runs at the rate of 5°C/min.

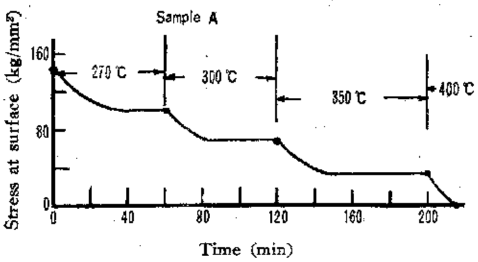

Fig. 2. Change of stress by heating according to the schedule of 270°C, 60 min-300°C, 60 min-350°C, 80 min-400°C, 20 min.

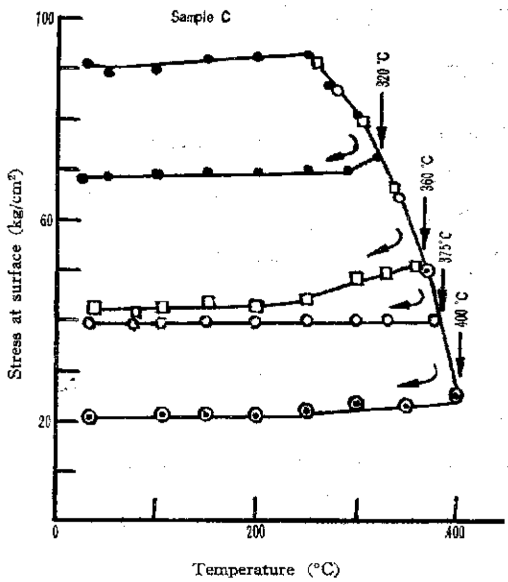

Fig. 3. Change of stress during heating (5°C/min)-cooling (2°C/min) cycles.

During cooling, stress did not change distinctly.

3. 4 Change of stress of the samples A and C at constant soaking temperatures is shown in Fig. 4 and 5 respectively. At 400°C, stress was released perfectly after 30 min of soaking. At lower temperatures, stress decreased rather rapidly at initial periods of soaking, and then attained to approximately constant values. The higher the soaking temperatures were, the lower were the final values.

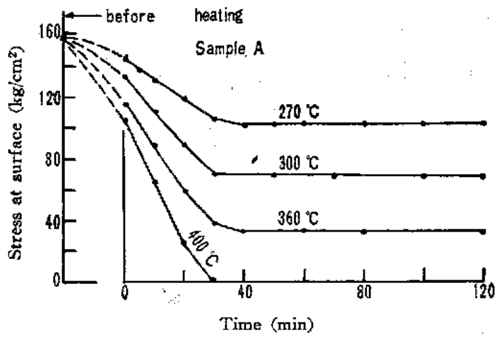

Fig. 4. Release of stress in the sample A by soaking at constant temperatures.

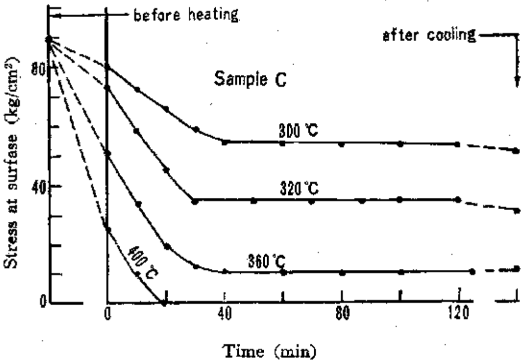

Fig. 5. Release of stress in the sample C by soaking at constant temperatures.

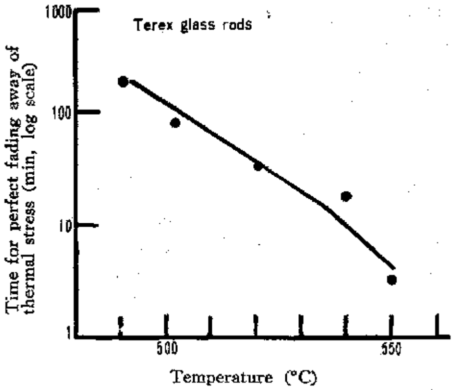

Fig. 6. Temperature vs. time for complete fading away of thermal stress of Terex glass rods (5 mm ϕ).

3. 5 For comparison, release of thermal stress in as-drawn Terex glass rods (5 mm ϕ) was observed. As is noted from Fig. 6, release of thermal stress by viscous flow took place in higher temperature range than those described in **3. 1～3. 4**.

4. Discussion and conclusion

It was confirmed that stress is caused by contraction (density increase) of glass in the irradated thin surface layer. Experimental results described above suggest that the stress release takes place by several mechanisms in different temperature ranges. Contribution of viscous flow of glass to the stress release is negligible at these temperatures which are considerably lower than the annealing point of the glass (about 555°C[4]).

Strict evaluation of activation energies in these mechanisms is impossible owing to complexity of the phenomenon. Indirect and approximate evaluation, however, is possible as follows:

When volume elements of glass in metastable (contracted) and stable (reformed) states are supposed, contracted elements translate to the stable state by thermal activation over the energy barrier E. As a first approximation, stress is presumed to be proportional to the number n of contracted elements. The transition probability of the elements is now supposed as $p=s\cdot\exp(-E/kT)$, where s, k and T are frequency factor, Boltsman constant and absolute temperature respectively. Similar presumption and mathematical treatment were given for thermal glow by trapped electrons in phosphors[5]. If p is, for example, 0.1/sec, n vanishes almost perfectly in several tens of second. This is considerably a short time in laboratory scale, and stress fades away "rapidly".

In Fig. 2, 4 and 5, rapid decrease of stress is observed at temperatures near 700°K.

For trapped electrons in various phosphors, the value of s is about $10^{7\sim10}$/sec[6]. In case of volume relaxation, which is presumably an atomic process, s is probably much smaller. Temperatures $T_{0.1}$ at which p is 0.1/sec, are shown in table 2 for some combinations of E and s. It is seen that, if $T_{0.1}$ =700°K and $s<10^{10}$/sec, E is not higher than 35 kcal/mol. This is low compared to that of viscous flow (about 100 kcal/mol[4]). Thus, it seems possible to conclude that breaking of network of glass does not contribute mainly to the stress relaxation. The stress relaxation presumably results from restoration of highly deformed chemical bond (restoration of bond angles or atomic distances between constituting atoms) and not from rearrangement of network forming atoms. It is also highly possible that this is true for mechanisms of stress build-up.

Table 2. Temperatures $T_{0.1}$ (°K) at which p is 0.1/sec, calculated for some combinations of E and s.

E (kcal/mol)	100	35	10
$s=10^{0}$/sec	22 000	7 700	2 200
10^{1}/sec	10 000	3 500	1 000
10^{10}/sec	2 000	700	200

Acknowledgment The authors wish to express their sincere thanks to Mr. I. Tsurumi, Kōbe Kōgyō Co., who kindly gave suggestion to this experiment.

References

1) T. Kishii, T. Ōmori, K. Ōoka, *J. Ceram. Assoc. Japan* **72** [11-1] 193 (1964).
2) K. Ōoka, T. Kishii, *J. Ceram. Assoc. Japan* **73** [4] 108 (1965).
3) K. Ōoka, T. Kishii, *J. Ceram. Assoc. Japan* **73** [7] 147 (1965).
4) T. Kishii, *Toshiba Review* **13** [6] 600 (1958).
5) J.T. Randall, M.H.F. Wilkins, *Proc. Roy. Soc.* (London) **A 184** 365 (1945).
6) for example, "Kotaibutsurikagaku (Physical Chemistry of Solids)" p. 477, Maruzen Publishing Co. (1956).

[Received Oct. 4, 1965]

紫外線照射により発生したガラスの応力の熱的緩和

大 岡 一 夫・岸 井 貫
(東京芝浦電気株式会社)

紫外線照射によって表面に応力を発生した硼珪酸ガラス (SiO_2 81, B_2O_3 12, Na_2O+K_2O 4.5, Al_2O_3 2.5 wt %) の小片を加熱し，応力が減少する過程を観察した．結果は次の通りであった：

1. 5°C/min の速度で加熱すると，応力は 250°C 位から緩和を始め，470°C で完全に消え，冷却しても再発生はしなかった．

2. 400°C に保持すると，応力は 30 分間で完全に消えた．250° ないし 360°C で定温保持すると，応力は始めの 30 分間で減少し，それ以後，ほぼ一定の値のままであった．これらの一定値は，保持温度が高い程小さく，また冷却後にもほとんど変化しなかった．

3. 上述の各温度は，このガラスの徐冷点 (約 555°C) よりかなり低いものであった．

以上の結果から次のように結論された：

1. 応力は，生起する温度域がそれぞれ異なるいくつかの機構によって緩和される．

2. 緩和機構の活性化エネルギーは 20～30 kcal/mol の間と推算され，粘性流動のそれ (約 100 kcal/mol) よりかなり低い．

3. それ故，応力緩和は，たとえばひずんだ化学結合 (結合角，原子間距離など) の回復の結果であって，網目構造を形成するイオンの再配置の結果ではないと推定される．

4. 上記と同じことは，応力発生の機構についても，恐らく成立つであろう．

(10/4/1965 受付)