10. Some Observations on "Thermally Released Current" in Glasses damaged by Ultra-violet Irradiation

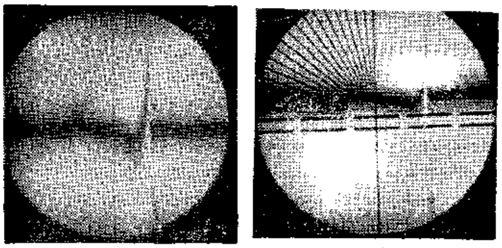
Stress in Glass Caused by Ultra-violet Irradiation (Part 7)

By

Kazuo ŌOKA and Tōru KISHII

(Tokyo Shibaura Electric Co., Kawasaki, Japan)

By heating glasses damaged by ultra-violet irradiation, "thermally released current" was observed[1]. In this note, results of detailed studies on the thermally released current are reported. Two kinds of damaged glasses were used as samples, namely; sample A (protection bulb made of Terex glass used for ordinary high pressure mercury discharge lamp, Composition; refer to 1)) and sample B (Pyrex glass manufactured by Corning Glass Works, SiO_2 81, B_2O_3 13, Na_2O 4, Al_2O_3 2 wt% used for high pressure mercury discharge lamp containing small amount of TlI). Photoelastic



(a) (b)

a) Sample A : Terex glass, b) Sample B : Pyrex glass

Fig. 1. Photo-elastic observation with quartz wedge of cross sections of bulb glasses.

observation with quartz wedge showed concentrated tension in the inner surface layers (Fig. 1). The method of "thermally released current" measurements was described in ref. 1). On both surfaces of a sample, In-Ga electrodes were painted, and they were connected to each other through Micro-micro-ammeter (Takeda Riken Co.). The sample was heated in a small electric furnace with the rate of about 30°C/min. Background current caused by electromotive force in the external circuit was about $10^{-9\sim-10}$ A at 200°C and 10^{-6} A at 500°C per 1 cm^2 of electrode area. "Thermally released current" superposed on it and as a result decrease or reversal of total current were observed.

Results of repeated measurements on as damaged samples are shown in Fig. 2. Positive sign in the figures indicate current flow from inner to outer surface through the sample. As was noted in ref. 1), the results were not reproducible. After washing with water, reversal or decrease of the currents occured only in the limited temperature range near 450°C (Fig. 3). After grinding off inner or outer surface layers, it was still the same (Fig. 4). After grinding off both inner and outer

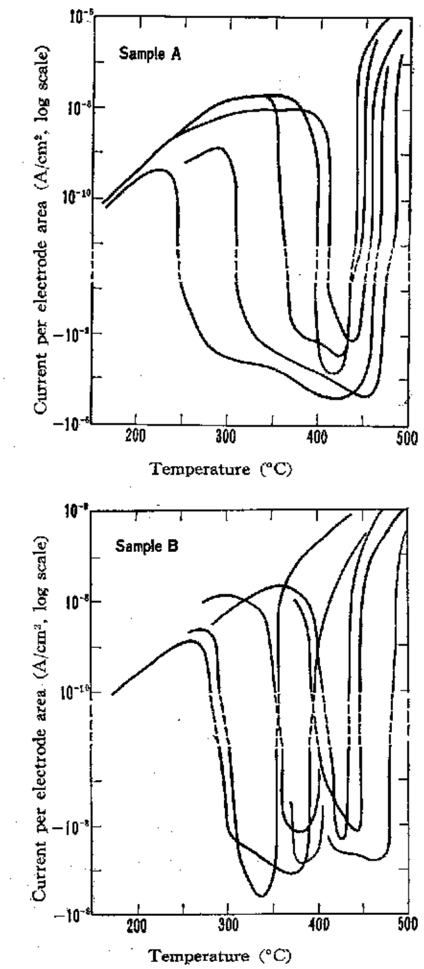


Fig. 2. Results of "thermally released current" measurements on the samples A and B (as damaged and received).

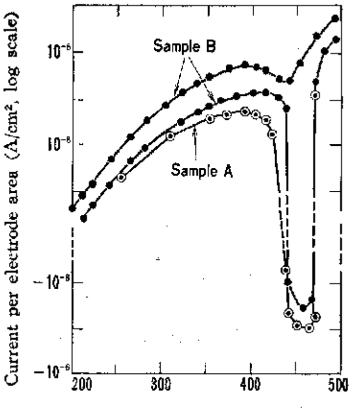


Fig. 3. Results of "thermally released current" measurements on washed samples.

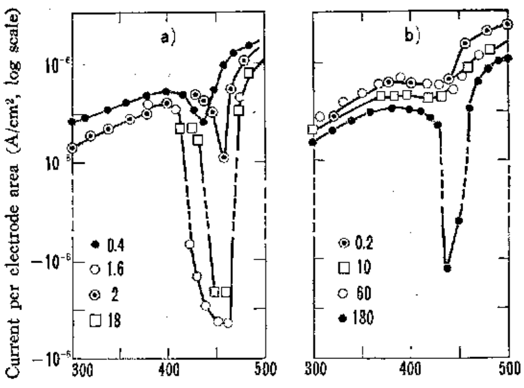


Fig. 4. Effects of grinding a) outer or b) inner surfaces of the samples B. Amounts of glass ground away (mg/cm²) are indicated in the figures.

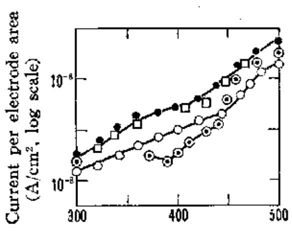


Fig. 5. Effects of grinding both outer and inner surfaces of the samples B on "thermally released current". Amounts of glass ground away (outer: inner surfaces in mg/cm²) were: ○ : (0.8 : 0.4), ◉ : (0.7 : 0.3), and ● : (0.3 : 0.1), respectively.

surfaces, however, reversal or decrease of the current were less distinct (Fig. 5).

It is clear from the results shown in Fig. 2 and 3, that the "thermally released current" is composed from at least two parts: by prior washing one of them vanishes and the other remains. The former one presumably originate in the extremely thin surface layer or is caused by adsorbed material.

"Thermally released current" of washed samples was estimated to be about 10^{-7} A/cm² and continued for about 100 sec. This corresponds to the space charge of about 10^{-5} Coulomb/cm², and if the charge exists only in the strained layer, it corresponds to about 10^{-4} Coulomb/cm². This is far greater than those observed in glasses irradiated by γ- or X-rays (for example, 6×10^{-7} Coulomb/cm² after 3×10^{7} roentgen irradiation by γ-ray[2)~5)]).

Accumulation of space charge of 10^{-4} Coulomb/cm² is expected, for example, in the cases described below: A) One pair of elementary charge $\pm$e exist in every ten SiO_4 tetrahedrons or BO_3 triangles arranged on the both sides of damaged layer, respectively, B) One tenth of Si^{4+}, B^{3+} or of O^{2-} ions in the damaged layer displace about 1 Å to the inner or the outer surfaces, respectively or C) Every SiO_4 tetrahedron and BO_3 triangle have dipole moments of e×(1 Å). If these structural changes presumed above really take place, they might be able to give rise to the compacion of the glass structure and build-up of stress in glass.

There are many possible mechanisms of the accumulation of the space charge in glass. They are, for example, a) Induced electric field in glass caused by anisotropic excitation or ionization of ions or scattering of electrons by ultra-violet ray and trapping of the electrons by structural imperfections in glass, and b) Atomic or molecular polarization, migration of alkali ions in the glass and absorption of foreign materials on the glass surfaces caused by the induced electric field. On the other hand, applied voltage of mercury lamp during lighting or charging up at inner surface of protection bulb by photoelectric effect of ultraviolet ray would have the similar effects. Moreover, with the build-up of stress in glass, migration of the alkali ions might take place[6)], and with the release of the stress by heating, backdiffusion of the ions might give rise to "thermally released current". Further studies are necessary to the complete understanding of the phenomenon.

References

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紫外線照射により損傷したガラスの“熱的緩和電流”についての観察

大岡一夫・岸井　貫
(東京芝浦電気株式会社)

高圧水銀灯の外管として使われ，紫外線照射により応力を発生したテレックス及びパイレックスガラスを加熱した時の熱的緩和電流の特性を観察した．損傷したままのガラスでは，熱的緩和電流が見られる温度域が 250° ないし 500°C の間にあり，また試料ごとに異なっていて再現性がなかった．試料を洗うと，この温度域が 450°C 附近の狭い範囲に局限され，また内表面あるいは外表面を削り落しても同様であった．しかし内外表面をともに削り落すと，緩和電流が顕著に減少した．緩和電流は電極面積 1 cm^2 当り $10^{-5\sim-4}$ クーロンの蓄積電荷に相当した．もしこれがガラス中の構成イオンの変移に原因するのであるならば，ガラスの構造ないし密度変化，従って応力発生を説明するのに十分な量である．しかし，電荷蓄積の原因として考えられるものがいくつかあり，特に応力発生そのものが原因であるかも知れないので，この現象を完全に理解するには，さらに研究を必要とする．

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