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VOLATILIZATION OF TYPE E BOROSILICATE GLASS

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The loss in weight due to volatilization of the Eutal alkali-free glass was determined over the temperature range of 1150—1450 °C in a stream of dry and moist nitrogen (p_{H_2O} = 20 kPa). The volatilization rate is strongly promoted by water vapour pressure. An analysis of the results indicates that the vapour pressure of HBO_2 ***at the melt surface is the decisive factor.***

INTRODUCTION

A survey of literary data on the volatilization of borosilicate glasses was presented in ref. [1] dealing with the phenomenon in connection with Simax glass (of the Pyrex type). As can be expected, volatilization of type E glass (so-called alkali-free glass for fibres) will differ as a result of the absence, or a very low content, of alkalies (1 wt. %) so that vaporization in the form of alkali metaborates ($NaBO_2$, KBO_2) is suppressed. On the other hand, the volatilization rate can be assumed to increase in moist atmosphere owing to the formation of HBO_2. An analogy can be expected with the behaviour of sodium tetraborate melts on the one hand and that of boric oxide on the other, as far as the effect of water vapour above the melt surface is concerned; in the former case, the water vapour has a very small effect, in the latter its effect being enormous [2, 3]. As has been demonstrated, this behaviour is in full agreement with a thermodynamic analysis of the reactions between the glass melt and water vapour.

The analogy was essentially proved correct by volatilization of the Simax glass. The results given in [1] were confronted with the data by other authors and found to be in a satisfactory agreement. In contrast to this, only scarce data on the volatilization of alkali-free glasses is available in the literature. Oldfield and Wright [4] also included one alkali-free glass having the composition 51.9 wt. % SiO_2, 24.9 % R_2O_3, 13.2 % CaO, 7.1 % B_2O_3 and 0.3 % $Na_2O + K_2O$ among the glasses they studied. The weight loss was measured by a thermobalance in a static atmosphere involving minimum convection. The volatilization losses of this glass, compared with the others (with the exception of standard soda—lime—silica glass and a borosilicate glass producing a cristobalite layer) were relatively low; after 25 h they amounted to approx. 95 mg/cm^2 at 1500 °C and to approx. 35 mg/cm^2 at 1300 °C. At both 1300 °C and 1400 °C, the dependence of weight loss on $\sqrt{t}$ was linear throughout the measurement (approx. 75 hours), at 1500 °C it was linear for 40 hours only; however, in all the instances the straight lines did not pass through the origin, intersecting the time ordinate at a comparatively large distance. On the assumption of a diffusion mechanism being involved, the activation energy calculated for the glass was 2.4 eV, i.e. 230 kJ/mol, i.e. a comparatively high value for diffusion in melt (similar values were also obtained for the other borosilicate glasses). No crystallization took place in the course of volatilization and only B_2O_3 was found in the condensate.

Further information on volatilization of type E glass melt was obtained from [5] where the volatilization loss of B_2O_3 was determined on two types of borosilicate glasses in the course of melting, while using various initial raw materials. In the case of a glass designated "alkali-free aluminoborosilicate E-glass" containing 10 wt. % B_2O_3, the losses were found to depend strongly on the type of raw material employed. When "clay" was used as the source of Al_2O_3, the losses of B_2O_3 were considerable, obviously as a result of liberation of H_2O by dehydration and subsequent formation of HBO_2.

Thermal exposure at 1400 °C had interesting results. Up to 5 hours the losses were roughly the same with the alkali-free and the alkali-borate glass of the 3 C—5 Na type (its composition was not specified). Longer exposures did not bring about additional losses of the 3 C—5 Na glass, which lost 4 wt. %, whereas with the E glass the loss kept increasing up to 9.5 % after 30 hours and then also remained unchanged. The alkali glass, originally containing 18.5 wt. % of B_2O_3, lost only 2.1 % B_2O_3 while altogether 8.7 % B_2O_3 was lost by the alkali-free glass with a lower boron content. According to analyses of the condensate, this contained 94 % of B_2O_3 and the rest, 6 %, of alkaline earth borates. The second glass liberated primarily $NaBO_2$ (the ambient atmosphere was not defined, assumed to be air).

On first sight, the fact that the alkali-borate glass with a higher B_2O_3 content than the alkali-free glas (with an almost half B_2O_3 content) showed less volatilization is surprising. The authors of the study in question explain this by structural differences between the two melts.

The data on the volatilization of borosilicate glass melts containing alkali oxides cannot be applied to alkali-free glasses owing to the significant role played by alkali oxides in the volatilization process.

EXPERIMENTAL

An Eutal glass having the composition 52.8 wt. % SiO_2, 8.3 % B_2O_3, 21.9 % CaO, 13.7 % Al_2O_3, 0.3 % MgO, 0.3 % Na_2O, 0.5 % K_2O, 0.38 % Fe_2O_3, 0.4 % TiO_2 was used in the experiments.

The glass was fused in a platinum boat so as to keep the level slightly below the top boat edge on melting. The fusing-in was effected at temperatures up to 1150 °C. The boat was about 4×1 cm in size, so that the surface area open to volatilization was about 4 cm^2 (always measured after concluded thermal exposure).

The specimen prepared in this way was weighed and introduced into a horizontal electric furnace with an inner corundum tube, which was tightly sealed and allowed the gaseous medium to be passed above the specimen in a controlled manner. The measurements were carried out in dry nitrogen (desiccated in a column filled with magnesium perchlorate), and in nitrogen humidified with water at controlled temperature in a moistening column. Use was made of nitrogen saturated with water vapour up to $p_{H_2O} = 20$ kPa. The rate of flow of the gaseous medium during the experiments was kept at 0.5 litre/min (at 20 °C) which, at the given tube diameter of 2.5 cm, corresponds to $v = 9$ cm/s (at 1300 °C).

Following thermal exposure at a temperature controlled with an accuracy of ±5 °C, the specimen was removed and its weight loss established. The result was expressed as the loss in mg/cm^2. Each measurement was carried out at least twice with a freshly fused-in sample.

To determine the temperature dependence, the losses due to volatilization were measured at four temperatures ranging from 1150 °C to 1450 °C. The time of exposure was always 4 hours. The results of the measurements for the dry and humid nitrogen atmospheres are plotted in Fig. 1.

The character of the time dependence was revealed by performing measurements at 1450 °C at one-hour intervals. The results are plotted in Fig. 2. Both diagrams indicate a very profound effect of water vapour on volatilization, in the sense of promoting it, in contrast to the results obtained with Simax glass [1].

The volatilization products condensed at the furnace outlet end were analyzed by flame photometry (alkalies), and using an ion-selective electrode (fluorine). The dry condensate contained 0.28 wt. % Na, the moist condensate (measurement with water vapour) contained 0.03 wt. % Na and 0.002 wt. % K. The fluorine content in the first specimen (originating from the refining agent CaF_2) was 0.038 wt. %.

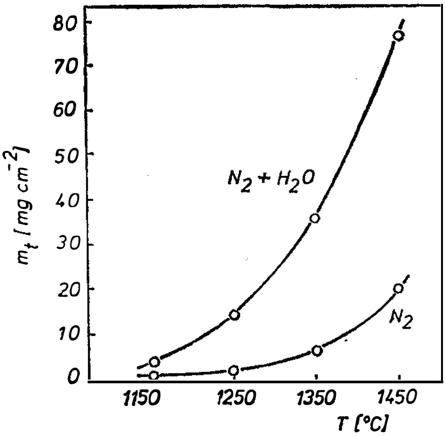

Fig. 1. Temperature dependence of volatilization losses for Eutal glass melt in dry and moist nitrogen (time of exposure 4 hours).

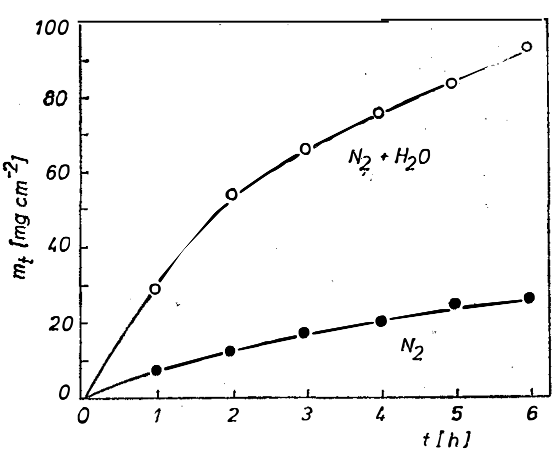

Fig. 2. Time characteristics of volatilization of Eutal glass melt in dry and moist nitrogen at 1450 °C.

DISCUSSION

The time dependence of the amount of substance vaporized from a static melt is given by a complex formula, including the rate of surface reaction and the coefficient of diffusion of the volatile component in the melt [6, 7]. If the surface process is very fast, the volatilization is controlled by diffusion in the melt and can be described by the familiar solution of the 2nd Fick law:

$$m_t = 2\,\Delta c \left(\frac{Dt}{\pi}\right)^{1/2}, \tag{1}$$

where m_t is the weight of the volatilized substance,
Δc — the respective concentration difference,
D — the diffusion coefficient, and
t — time.

If the experimentally established dependence $m - \sqrt{t}$ is linear and passes through the origin, the assumption of a rapid surface reaction has been met and the slope of the straight line can be considered to be proportional to $\sqrt{D}$.

The temperature dependence of the amount vaporized may then be expressed, using equation (1), by substituting $D = D_0 \exp(-E/RT)$, obtaining

$$\frac{m_t}{\sqrt{t}} = \frac{2\,\Delta c}{\sqrt{\pi}}\,[D_0 \exp(-E/RT)]^{1/2} \tag{2}$$

and

$$\log \frac{m_t}{\sqrt{t}} = \text{const.} - \frac{E}{2\,.\,2.303RT}. \tag{3}$$

The slope of the relationship of the left-hand side of the equation on $1/T$ then allows the activation energy E of diffusion to be calculated.

The time dependence of volatilization losses for the Eutal glass is shown in Fig. 3; the assumption of a linear relationship between m_t and $\sqrt{t}$ is met only

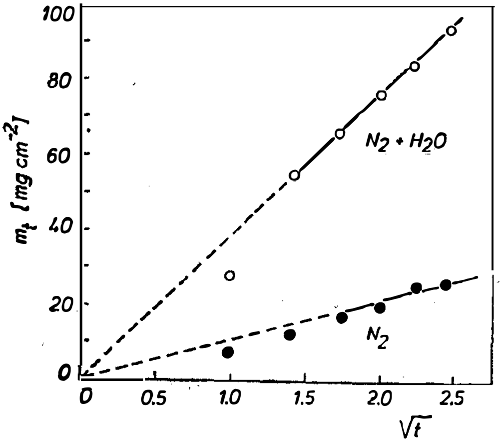

Fig. 3. Volatilization losses vs. $\sqrt{t}$ *at 1450 °C.*

partially, since distinct deviations appear after short-term thermal exposure. If the activation energy E is calculated according to equation (3) using the values obtained after 4-hour exposures, the resulting value of $E_D = 406$ kJ/mol for the medium of humid nitrogen appears to be inadequately high for diffusion in a melt. The dependence of log $(m_t/\sqrt{t})$ on $1/T$, used in the calculation for both media, is shown in Fig. 4. In both cases the relationship can be regarded as being linear, even though both series of points show a mild but opposite curvature. In the case of dry nitrogen, the slope and thus also the activation energy are still somewhat higher, $E_D = 420$ kJ/mol; however, the difference is negligible, being within the limits of measuring errors.

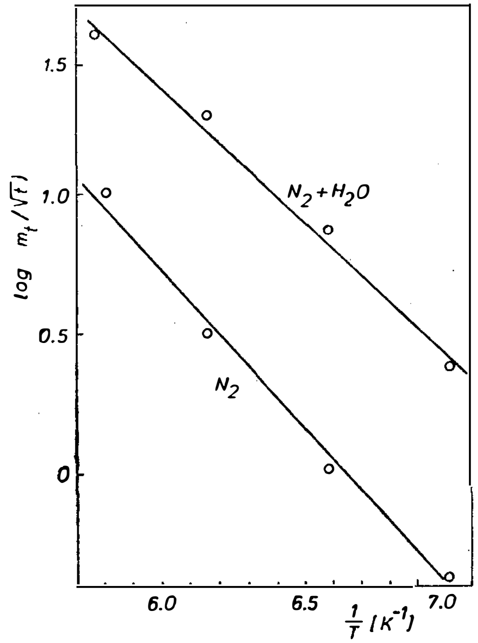

Fig. 4. Logarithm of volatilization loss after 4 hours vs. reciprocal temperature in K.

The very steep temperature dependence of volatilization losses indicates to the involvement of an additional temperature-dependent parameter apart from the diffusion coefficient, most probably the vapour pressure. The initial volatilization rate should be proportional to the vapour pressure difference according to the equation [8],

$$j = D_g(p_e - p_0)\, M/RT\delta \qquad [\text{g cm}^{-2}\,\text{s}^{-1}], \qquad (4)$$

where j is the diffusion flux density of vapours from the melt surface (i.e. the volatilization rate),

D_g — the diffusion coefficient of vapours in the boundary layer of gases δ in thickness,

M — the molecular weight of the vapours,

$(p_e - p_0)$ — the difference between equilibrium and ambient vapour pressure.

The relationship between equilibrium vapour pressure and temperature is described by the equation

$$\ln p = -\frac{\Delta H}{RT} + C, \tag{5}$$

where ΔH is the heat of evaporation, and C is a constant.

If, in the first approximation, the initial rate of volatilization is considered to be equal to the value calculated from the four-hour exposure, and if the value is directly proportional to the vapour pressure of the volatile component, the temperature dependence of the volatilization rate defined in this way allows the value of ΔH to be calculated by means of equation (5); the slope of the linear dependence will be identical with Fig. 4, but the result will differ by a factor of 2, as follows from the derivation of equation (3). For the volatilization in question, one thus obtains $\Delta H = 203 - 210$ kJ/mol.

According to various literary data, the vaporization heat of B_2O_3 amounts to 325—365 kJ/mol; the reaction heat of the formation of HBO_2 from B_2O_3 (l) and H_2O (g) is 170—188 kJ/mol. The value of 203 kJ/mol approaches the latter data; in that case it would not be the heat of volatilization, but that of the reaction

$$1/2\, B_2O_3\,(l) + 1/2\, H_2O\,(g) = HBO_2\,(g).$$

The equilibrium constant K of this reaction is proportional to the vapour pressure of HBO_2, and the equation for the temperature dependence of $\ln K$ is formally identical with equation (5) for $\ln p$ except that ΔH represents the reaction heat.

These comparisons indicate that the volatilization takes place mostly in the form of HBO_2. The equilibrium pressure of the substance at the boundary will be attained in a moist atmosphere, while in a dry one the pressure of HBO_2 vapour at the boundary would be very low, being given only by the content of H_2O dissolved in the glass, and/or by traces of water vapours in the carrier gas. A simple calculation shows that for the maximum amount vaporized in a dry medium (26 mg/cm^2 per 6 h), if only HBO_2 alone were involved, the water concentration in glass would correspond to 0.25 wt. %. According to L. Němec [9], the solubility of water in borosilicate glasses exceeds that in soda-lime-silica ones; Eutal was found to contain about 0.1 wt. %. However, one should take into account that in addition to HBO_2 vapours, also B_2O_3 molecules volatilize in a dry medium, beside alkali metaborates from the small amounts of alkalies contained in the glass.

These considerations are only qualitative in their significance, having been arrived at with the use of considerable simplifications. Moreover, mention should be made of one additional phenomenon which influenced the measuring results in an uncontrollable way: bubbles were formed at the walls of the platinum boat during the thermal exposure, and sometimes even caused the melt to flow over the edges. Such measurements had to be eliminated. However, the bubbles escaping from the melt during the measurement were responsible for convective agitation, and thus for a higher volatilization loss.

The more extensive volatilization of Eutal glass compared to Simax is in agreement with the findings by Oldfield and Wright [4b]. On recalculating the data it was shown that glass A, used by the authors mentioned, containing 16.2 % B_2O_3 and 5.9 % $Na_2O + K_2O$, exhibited a loss of 2.5 mg/cm^2 after 4 hours at 1400 °C, whereas glass E with 7.1 % B_2O_3 and 0.3 % K_2O lost approx. 10 mg/cm^2 during the same time, i.e. four times as much. This fact is not discussed nor specifically mentioned in study [4b], except for a mention of extensive formation of a cristobalite layer on the surface of glass A. A similar result of study [5] was mentioned in the introduction; the authors offer an explanation based on a difference in the structures of alkali-containing and alkali-free borosilicate melts. This conclusion can be accepted while adding that the different structures of the two melts (a weaker bond of boron in E glass resulting from coordinated arrangement with three oxygen atoms) may lead to a more ready liberation of B_2O_3 for its reaction with water, whereas the more firmly bound B_2O_3 (coordination 4) in Simax slows down the surface reaction or desorption of B_2O_3 and thus also the entire volatilization process, additionally suppressing it by forming the cristobalite layer.

CONCLUSION

In spite of a very low content of alkalies and a relatively low content of B_2O_3, melts of Eutal glass may exhibit considerable volatilization losses in air atmosphere in the presence of water vapour which increases the volatilization rate by a factor of more than three.

The different behaviour of Simax glass melts as compared to Eutal glass melt is attributed to the difference in the content of alkalies and to the formation of a cristobalite layer in the case of Simax.

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TĚKÁNÍ BORITOKŘEMIČITÉ SKLOVINY TYPU E

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Byly stanoveny hmotnostní ztráty těkáním bezalkalické skloviny Eutal v rozmezí 1150 až 1450 °C, a to v proudu suchého a vlhkého dusíku (P_{H_2O} = 20 kPa). Sklo se nacházelo v Pt lodičkách, naplněných až po okraj, povrch vystavený těkání činil cca 4 cm^2. Úbytek těkáním byl stanoven vážením.

Ke zjištění teplotní závislosti byly vzorky exponovány při 4 teplotách, s dobou expozice 4 h. Výsledky jsou uvedeny v obr. 1. Ke stanovení charakteru časové závislosti bylo provedeno měření při 1450 °C(obr. 2). Z obou obrázků je patrný výrazný vliv vodní páry na těkání. Kondenzát obsahoval 0,28 hm. % Na, ve vlhkém N_2 obsahoval 0,03 % Na. Hlavní těkající složkou je tedy B_2O_3, resp. kys. boritá.

Jestliže je povrchový děj rychlý, vypařování je řízeno difúzí v tavenině podle vztahů (1—3). Závislost ztrát těkáním na $\sqrt{t}$ by pak měla být lineární. Tento předpoklad je splněn pouze částečně (obr. 3), při krátkých časech jsou patrné odchylky. Jestliže přesto provedeme výpočet aktivační energie E podle vztahu (3), dostaneme hodnoty 406 a 420 kJ/mol pro prostředí N_2 a $N_2 + H_2O$ (obr. 4). Strmá teplotní závislost svědčí o tom, že se při těkání uplatňuje jako další teplotně závislý parametr tlak par. Je ukázáno, že výsledky jsou zhruba v souladu se závislostí rovnovážného tlaku par na teplotě (vztah 5), zejména v případě prostředí $N_2 + H_2O$, kdy se jako reakční produkt na rozhraní tvoří HBO_2. Výsledky tedy jsou v souladu s běžnou představou o mechanismu vypařování B_2O_3 ve formě HBO_2, jestliže je k dispozici vodní pára. Tím je proces vypařování podstatně urychlen.

Ztráty těkáním ze skloviny Eutal mohou přes velmi nízký obsah alkálií v tomto skle a poměrně nízký obsah B_2O_3 dosahovat značných hodnot v atmosféře s vodní parou, jež zvyšuje rychlost těkání více než trojnásobně. Rozdílné chování skloviny Simax ve srovnání se sklovinou Eutal je přičítáno rozdílu v obsahu alkálií a tvorbě cristobalitové vrstvy v případě Simaxu [1].

Obr. 1. Teplotní závislost ztrát těkáním skloviny Eutal v suchém a vlhkém dusíku (doba expozice 4 h).

Obr. 2. Časová charakteristika těkání skloviny Eutal v suchém a vlhkém dusíku při 1450 °C.

Obr. 3. Závislost ztrát těkáním na $\sqrt{t}$ *při 1450 °C.*

Obr. 4. Závislost log ztrát těkáním po 4 h na reciproké teplotě v K.

УЛЕТУЧИВАНИЕ БОРОСИЛИКАТНОЙ СТЕКЛОМАССЫ ТИПА Е

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Были установлены потери в весе, вызванные улетучиванием, бесщелочной стекломассы Eutal в пределах температуры 1150—1450 °C, а именно в потоке сухого и влажного азота (P_{H_2O} = 20 кПа). Стекло находилось в Pt лодочках, заполненных до краев, поверхность, подвергаемая улетучиванию, составляла приблизительно 4 см². Потеря в весе была установлена взвешиванием.

Для установления температурной зависимости образцы подвергались четырем температурам, время экспозиции 4 часа. Полученные результаты приводятся на рис. 1. Для определения характера временной зависимости проводили измерения при температуре 1450 °C (рис. 2). Из обоих рисунков видно резкое влияние водяного пара на улетучивание. Конденсат содержал 0,28 % по весу Na, во влажном N_2 — 0,03 % по весу Na. Следовательно, основным улетучивающим компонентом является B_2O_3, или борная кислота.

В случае быстрого протекания поверхностного процесса испарение управляется диффузией в расплаве согласно отношениям (1—3). В таком случае зависимость потерь улетучиванием от $\sqrt{t}$ должна быть линейной. Данное предположение выполняется только отчасти (рис. 3), при кратких отрезках времени видны отклонения. Однако если все-таки проводить расчет энергии активации E согласно отношению (3), то получим величины 406 и 420 кдж/мол в случае среды N_2 и $N_2 + H_2O$ (рис. 4). Резкая температурная зависимость является свидетельством того, что при улетучивании находит применение в качестве дальнейшего температурно зависимого параметра давление пара. Было доказано, что результаты находятся в общем согласии с зависимостью равновесного давления пара от температуры (отношение 5), именно в случае среды $N_2 + H_2O$. Следовательно, результаты находятся в согласии с общим представлением о механизме испарения B_2O_3 в виде HBO_2 в том случае, когда присутствует водяной пар. Таким образом процесс испарения существенно ускоряется.

Потери, вызванные улетучиванием из стекломассы Eutal даже при весьма низком содержании щелочей в данном стекле и сравнительно низкое содержание B_2O_3 могут достигать значительных величин в среде с водяным паром, который повышает скорость улетучивания больше, чем в три раза. Различное поведение стекломассы Simax в сопоставлении со стекломассой Eutal объясняется разным содержанием щелочей и образованием кристобалитного слоя в случае стекломассы Simax [1].

Рис. 1. Температурная зависимость потерь улетучиванием стекломассы Eutal в сухом и влажном азоте (время экспозиции 4 часа).

Рис. 2. Временная характеристика улетучивания стекломассы Eutal в сухом и влажном азоте при температуре 1450 °C.

Рис. 3. Зависимость потерь улетучиванием от $\sqrt{t}$ при 1450 °C.

Рис. 4. Зависимость log потерь улетучиванием после 4 часов от обратной температуры в K.