# THE CHEMICAL, PHASE AND ENTHALPY BALANCE OF CHANGES IN THE PRE-HEATED BATCH FOR THE EUTAL GLASS

# I. Determination of the mass balance of the escape of gas reaction products

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The mass balance of gaseous reaction products  $(CO_2, H_2O)$  and gaseous forms of boric acid) escaped during the process of heating of the pressed Eutal glass batch in the range of  $\langle 25 \,^{\circ}C, 800 \,^{\circ}C \rangle a \rangle$  in the stream of N<sub>2</sub> and b) in the stream of natural gas combustion products of the approximate composition as 70 vol. % N<sub>2</sub>, 20 vol. % H<sub>2</sub>O, 10 vol. % CO<sub>2</sub> was determined. The termogravimetry, atomic emission spectrometry, DTA and X-ray diffraction techniques were used in this investigation. This paper is focused on determination of the boric oxide mass decrease in the pre-heated batch as a temperature function that is due to reactive vaporization in the presence of water vapour. The total relative loss of boric oxide from the pressed batch with an initial content of B<sub>2</sub>O<sub>3</sub> equal to 6.8% is about 14.5% when the batch is pre-heated in the stream of combustion products whereas pre-heating the batch in the nitrogen stream results in a loss of 6.8%. The value of the B<sub>2</sub>O<sub>3</sub> loss depends consequently upon the content of structural water in the batch components, as well as upon the water in the natural gas.

#### 1. INTRODUCTION

This paper (both parts) can be seen as a contribution to judging the possibility of the decrease or the removance of unfavourable work, economical and ecological consequences in production of borosilicate Eutal glass. The possibility of using residual enthalpy of the combustion products flowing from a melting aggregate for pre-heating the pressed Eutal glass batch is discussed. The data of both the phase analysis and the temperature function of enthalpy change of the heated pressed batch between 25 °C and 800 °C were obtained by using of the experiment. with laboratory modelled heatings of the pressed Eutal glass batch that were accomplished in the stream of gaseous carrier of natural gas combustion products at the temperature growth rate  $10 \, {}^{\circ}\text{C}$ . min<sup>-1</sup>. Together with the analysis of chemical and enthalpy changes the temperature dependence of the  $B_2O_3$  loss from the pressed batch as a consequence of reactive evaporating in the presence of water steam was determined. In this paper determination of the mass balance of gaseous reaction products is presented. The gases were released from the heated pressed Eutal glass batch in the stream of an approximate combustion products composition. We payed heed primarily to the values of the mass  $B_2O_3$  decrease from the heated batch.

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## 2. EXPERIMENTAL

# 2.1. Sample preparation

Pressed cylindrical pieces made of the Eutal glass batch (the diameter d = 11.5 cm; the height h = 11 mm; the mass  $\approx 2$  g; the density  $\varrho = 1.7 - 1.8$  g/cm<sup>3</sup>; the pressing pressure p = 0.8 MPa) were used for experimental heatings. The raw-material and oxide composition of the Eutal glass is given in Table I. Before each pressing was prepared, 3 mass % of water was added to the batch to make the batch easily pressable.

Composition of	the Eutal batch	Composition of the Eutal glass			
Raw-material	w/mass %	Oxidə	$w   \mathrm{mass} \ \%$		
Sand Kaolin* Calcite Dolomite H <sub>3</sub> BO <sub>3</sub> Fluorite Sulfate H <sub>2</sub> O (1)	23.65 30.76 15.14 13.12 12.21 1.86 0.26 3.0		$53.0 \\ 14.4 \\ 8.2 \\ 0.3 \\ 0.3 \\ 18.3 \\ 4.4 \\ 0.2 \\ 0.5$		

Table I

\* Kaolin was primarily a mixture of kaolinite, illite and SiO<sub>2</sub>.

# 2.2. The experimental apparatus

A determination of the water steam influence upon the process in the batch, when its temperature is increased, was required in order to explore the possibility of using of the waste heat of natural gas combustion products for direct preheating of the Eutal batch before inserting it into the melting aggregate. Therefore two series of the pressed batch heatings were accomplished under the conditions as follows:

a) in a gaseous mixture stream of the average composition of combustion products as  $\varphi(N_2) = 70$  vol. %,  $\varphi(H_2O) = 20$  vol. %,  $\varphi(CO_2) = 10$  vol. %,

b) in a stream of  $N_2$ .

The used pressed batch has some advantageous properties when compared with powdered batch such as: prevention of charge segregation, higher heat conductivity, improved heat transfer, decrease of losses due to dispersion, etc.

The scheme of the heating apparatus is in Fig. 1. Nitrogen and carbon dioxide were taken away from pressure containers (1) and (2). The gas flow  $\varphi$  was controlled by flow-meters (3) and (4) ( $\varphi(N_2) = 0.23 \text{ dm}^3 \cdot \text{min}^{-1}$ ,  $\varphi(CO_2) = 0.04 \text{ dm}^3 \cdot \text{min}^{-1}$ ). The gases were mixed in the T-tube with a frit (5). The gaseous mixture was saturated to the required content with water steam ( $p(\text{saturated } H_2O \text{ steam}, 60 \text{ °C}) \approx 20 \text{ kPa}$ ) in steam producer (8) and then proceeded through a pipe (10) into the SiO<sub>2</sub> glass tube (11) that was fixed in the axis of the horizontally mounted furnace with a Kanthal winding (13). Samples were inserted into the Pt-boat (14). The temperature of samples was measured with the Le Chatelier thermometer (16)connected with thermo-regulator Chinoterm LP 849 (17). Once the required maximum temperature of sample heating was achieved the CO<sub>2</sub> feed was closed and the steam producer was disconnected by values (6) and (7). The sample was cooled in pure nitrogen stream that removed water steam and other reaction gaseous products from the space around the sample. Thus temperature decrease of the sample was accelerated. The sample heating rate was 10  $^{\circ}$ C. min<sup>-1</sup> in temperature intervals of 25 °C — t ( $t \in \langle 200 \text{ °C}, 800 \text{ °C} \rangle$ ). During heating of the samples the gaseous reaction products (boric acid, water steam and carbon dioxide) escaped from the heated samples. Masses of the products were quantitatively determined  $(m_{\mathbf{g}}(X) = -\Delta m(X)$  — the mass decrease of the component X of the sample). Boric acid and its solution condensed first on the cooler parts of the tube (11), next on the interconnecting parts of the apparatus and the rest was captured in the absorber (that is a shallow dish filled with glass balls (18) and cooled with a mixture of solid  $CO_2$  and ethylalcohol).  $CO_2$  was absorbed in the saturated water solution of  $Ba(OH)_2$ .



Fig. 1. The laboratory device applied to the heatings of pressed samples of Eutal glass batch and its subsystems in the flowing gas atmosphere.

2.3. Determination of  $m_{f}(B_2O_3)$ 

After the furnace was cooled down, the relevant glass parts of the apparatus were precisely (quantitatively) clean-washed in order to get the condensed boric acid and its solution into a graduated glass. Then the formal concentration of  $B_2O_3$  was determined by atomic spectral analysis.

# 2.4. Determination of $m_g(CO_2)$ and $m_g(H_2O)$

The masses of  $CO_2$  and of water steam escaped during the heating of pressings as a consequence of chemical reactions among the batch components or due to their thermic decomposition were determined according to the two procedures:

#### a) Heating in the stream of nitrogen

The filtered and washed BaCO<sub>3</sub> precipitate from the CO<sub>2</sub> absorber was dissolved in 20 cm<sup>3</sup> of 0.1 M HCl. The value of  $m_g(CO_2)$  was determined by titration of the surplus acid with the 0.1 M solution of NaOH. The value of  $m_g(H_2O)$  was obtained

by subtraction of the sum of  $m_g(B_2O_3)$  plus  $m_g(CO_2)$  from the total mass decrease of a pressing (the mass difference before heating and after it determined by weighing).

b) Heating in the combustion products stream

The mass balance of  $CO_2$  and water escaped from pressings was in this case complicated by presence of both compounds in the gaseous mixture flowing around pressings. The values of  $m_g(CO_2)$  and  $m_g(H_2O)$  were estimated on the basis of the known Eutal glass batch composition (Table I) with the use of the mass fractions



Fig. 2. The series of TG-curves of pressed batch for the Eutal glass pre-heated in the gas atmosphers with the composition of natural gas combustion products within 25 °C - t;  $t \in \langle 200 \text{ °C}, 800 \text{ °C} \rangle$ .

of CO<sub>2</sub> and of water in the cooled pre-heated pressings (determined by the TG analysis (temperature range  $\langle 25 \, ^{\circ}C; 1000 \, ^{\circ}C \rangle$ )). The content of water in the cooled down pressings was corrected by subtracting of the mass increase that was due to a partial rehydratation in the process of cooling off the samples in the apparatus. The mass increase after heating was also estimated by the TG analysis. The values  $m_g(CO_2)$  and  $m_g(H_2O)$  are specified by the following equations:

$$m_{g}(CO_{2}) = m_{0} \cdot [w_{0}(CO_{2}(\text{calcite})) + w_{0}(CO_{2}(\text{dolomite}))] - (1)$$
  
- m. [w(CO\_{2}(\text{calcite})) + w(CO\_{2}(\text{dolomite}))],

$$m_{g}(H_{2}O) = m_{0} \cdot \sum_{X} w_{0}(H_{2}O(X)) - m \cdot [\sum_{X} w(H_{2}O(X)) - w(H_{2}O, \text{ rehydrated})].$$
 (2)



Fig. 3. The series of DTA-curves concerning the pressed Eutal glass batch pre-heated in the flowing gas atmosphere with composition of natural gas combustion products.

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 $w_0(Y(X))$  and w(Y(X)) represents the mass fractions of a compound Y (CO<sub>2</sub> or water) pertaining to a raw-material X of a pressing before heating (the sample mass is  $m_0$ ) and after heating respectively (the sample mass is m). The values  $m_g(Y)$  may be distorted due to the additional escape of gaseous components from pressings while they are cooled down. Further mistakes may be caused by a simultaneous escaping of gaseous components during the TG analysis of cooled off samples in the range of  $\langle 25 \, ^\circ C, 1000 \, ^\circ C \rangle$ . The quantity  $w(H_2O)$ , rehydrated) was used to check the content of free  $B_2O_3$  in the samples after the heating was finished.

In Fig. 2. and 3. there are the TG and DTA curves of samples analyzed after heating in the range  $\langle 25 \, ^{\circ}C, 800 \, ^{\circ}C \rangle$ . The values of  $m_{g}(CO_{2})$  and  $m_{g}(H_{2}O)$  were obtained through the analysis of peaks on the TG curves by using equations (1) and (2).

#### 2.5. Other methods used

Determination of the mass balance of gaseous products was combined with difference scanning calorimetry (DSC) for quantitative enthalpy analysis of phase changes during the heating of samples. X-ray, and also DTA and TG analyses were used for identification of phases.

# 3. DISCUSSION OF RESULTS

The loss of  $B_2O_3$  from the Eutal glass batch in the presence of water steam is caused by the reactions that may be written down in these simplified schemes:

$$B_2O_3 \text{ (cond.)} + H_2O \text{ (g)} \rightarrow 2 \text{ HBO}_2 \text{ (g)},$$
 (3)

$$B_2O_3 \text{ (cond.)} + 3 H_2O (g) \rightarrow 2 H_3BO_3 (g), \qquad (4)$$

$$H_3BO_3(s) \rightarrow H_3BO_3(g).$$
 (5)

According to [1] the pressure of boric acids vapour generated by the first two reactions considerably increases with the increase of both temperature and pressure of water steam around the condensed  $B_2O_3$ . Authors of the paper [1] assumed that molecules of HBO<sub>2</sub> existed in gaseous phase in the range of  $\langle 1200 \, ^\circ C, 1300 \, ^\circ C \rangle$ . They also supposed a presence of  $H_3BO_3$  molecules in gaseous phase at lower temperatures. According to [2] trimer (HBO<sub>2</sub>)<sub>3</sub> is produced at 1250  $^\circ C$  through the reaction of condensed  $B_2O_3$  with water steam. The leakage of boric compounds from the condensed phase of  $B_2O_3$  was studied in both papers mentioned above under conditions that modelled dosing of charge into a melting tank, initial producing of glass melt and the main  $B_2O_3$  losses. (The total  $B_2O_3$  loss in the production of borosilicate glasses is given between 15 and 30 % of initial  $B_2O_3$  content in a batch [3]).

The  $B_2O_3$  loss determination results of the pressed Eutal glass batch and its subsystems versus temperature are given in Table II or in Fig. 4.

The losses of  $B_2O_3$  from the Eutal glass batch pressings of the composition given in Table I are presented in Table II, columns a, b and the losses of  $B_2O_3$  from the modified system pressings are presented in Table II, column d. The samples were heated in temperature intervals of 25 °C — t ( $t \in \langle 200 \text{ °C} \rangle$ ). For comparison in column c are presented the losses of  $B_2O_3$  measured in [4] for heatings of a similar composition batch in a static air atmosphere. These losses are lower when compared to the losses of the pressed batch heatings in the flowing atmosphere.

Table II
The balance of $ m B_2O_3$ leakage from the pressed Eutal glass batch and from subsystems as a function
of temperature of heating

Serier a	a 6.76		b 6.76		o 10 [4]		d 6.76		е 15.85	
t/°C	a	ь	a	b	a	b	a	ь	a	Ь
200 300 400 450 550 600 700 750 200	2.3 3.2 8.0 13.0 12.9 13.4	0.16 0.22 0.54 0.88 0.87 0.91	3.9 4.5 5.7 8.8 7.4 6.8	0.26 0.30 0.39 0.60 0.50 0.46	1.8 2.9 3.6 4.8 4.5	0.18 0.29 0.36 0.49 0.46	3.8 9.5 10.3 10.1 14.0 14.0	0.26 0.64 0.70 0.68 0.95 0.95	9.2 8.6 10.6 10.5 9.8 8.3	1.46 1.36 1.68 1.66 1.55 1.32
800	14.4	0.97	6.8	0.46	5.6	0.57	17.4	1.18	7.2	1.14

 $a \dots (m_g(B_2O_3)/m_0(B_2O_3))/\%, b \dots (m_g(B_2O_3)/m_0)/\%, \alpha \dots w_0(B_2O_3)/mass \%$ 

 $w_0(B_2O_3) = m_g(B_2O_3)/m_0$  — analytically determined initial mass fraction of  $B_2O_3$  in the batch. a... the pressings made of the Eutal glass batch of the composition given in Table I. The pressings were heated in the gaseous mixture stream of approximate composition of natural gas combustion products (70 vol. % of  $N_2$ , 20 vol. % of  $H_2O$ , 10 vol. % of  $CO_2$ .)

b... the pressings made of the Eutal glass batch were heated in pure nitrogen.

c... the unpressed samples of the Eutal batch were heated in static air atmosphere. Temperature increase rate was  $5 \,^{\circ}$ C. min<sup>-1</sup> (results of V. Tatevosjan's measurement [4]).

d... the pressings of modified glass batch containing 7.51 mass % of Ca(OH)<sub>2</sub> and 7.51 mass %, of CaCO<sub>3</sub> were heated in the atmosphere of combustion products composition.

e... the pressings of the binary system of kaolin-boric acid. The ratio of Al<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> content in the system is as equal as in the Eutal glass  $(w_0(Al_2O_3)/w_0(B_2O_3) = 1.76)$ .

The relative loss of  $B_2O_3$  versus temperature for the systems mentioned earlier is given in Fig. 4. (the curves are denoted in consistence with the legend to Table II). The influence of gaseous combustion products composition upon the degree of the  $B_2O_3$  loss from the batch was determined on the basis of valorization of the Eutal glass batch heating results in the stream of pure N<sub>2</sub> (column b in Table II, curve b in Fig. 4.) and in the gas stream of an average composition of the combustion products under the same conditions (column a in Table II, curve  $\alpha$  in Fig. 4.).

The intensity of boric acids evaporation from the Eutal batch heated in the stream of  $N_2$  increases in the temperature intervals where the structurally bound water is released from boric acid and kaolin:

In the range of  $\langle 100^{\circ}$  C, 250° C $\rangle$  water steam is predominantly generated by the thermic decomposition of boric acids H<sub>3</sub>BO<sub>3</sub> and HBO<sub>2</sub>. The loss from the total amount of water in the batch is 100.  $m_{g}(H_{2}O)$ , boric acid) $/m_{0}(H_{2}O) \approx 45 \%$ .

In the range of  $\langle 450 \,^{\circ}\text{C}, 700 \,^{\circ}\text{C} \rangle$  kaolinite (illite) is dehydrated — 100.  $m_g(\text{H}_2\text{O}, \text{kaolin})/m_0(\text{H}_2\text{O})) \approx 30 \,\%$ .

In the beginning of heating the batch moisture is evaporated — 100.  $m_g(H_2O_r)$ , humidity)/ $m_0(H_2O) \approx 25\%$ .

The total relative loss of  $\dot{B}_2O_3$  from the batch heated in the N<sub>2</sub> atmosphere in the temperature range of (25 °C, 800 °C) is 100 ·  $m_g(B_2O_3)/m_0(B_2O_3) \approx 7 %$ . The temperature dependence of  $B_2O_3$  loss from batch pressings (curve b in Fig. 4.)



Fig. 4. Relative loss of  $B_2O_3$  from the heated pressed Eutal glass batch versus temperature: the rate of temperature growth is  $10 \,^{\circ}C \cdot min^{-1}$ 

a) heatings of pressed batch samples in the gas stream of combustion products composition,

b) heatings of pressed batch samples in the stream of  $N_2$ ,

c) the results of the paper [4],

d) heatings of the pressed batch samples of modified composition (the batch contains 7.51 % calcite and 7.51 % Ca(OH)<sub>2</sub>).

has a seeming maximum at 600 °C evidently due to an imperfection of the used method (the further  $B_2O_3$  has escaped, inside pressings were cooled down). The shape of this curve is effected likewise by the generation of borates because the reactive vaporization of borate compounds with water steam depends primarily upon the free B<sub>2</sub>O<sub>3</sub> content in a pre-heated pressing and to a considerably lower degree upon the content of  $B_2O_3$  that is bound in borates. The loss of  $B_2O_3$  in the process of tablet heating in the combustion products stream within the entire temperature range is higher than that in the stream of  $N_2$ . The total loss of  $B_2O_3$ related to its original content is 100.  $m_g(B_2O_3)/m_0(B_2O_3) \approx 14.5\%$ . Water steam not only increases the loss of  $B_2O_3$  in the form of boric acid but also accelerates reactions of boric compounds in the batch with other components (calcite, dolomite, metakaolinite). A catalytic effect of water steam upon the carbonates decomposition was also observed. Therefore the rate of the free  $B_2O_3$  content decrease in the Eutal glass batch heated in the combustion products stream is considerably higher than in the stream of  $N_2$ . The  $B_2O_3$  reaction rate in the batch with water steam can be judged from the shape of the  $B_2O_3$  loss curve (curve a in Fig. 4.). The slope of the curve is the highest in the temperature range of  $\langle 300^{\circ}C, 600^{\circ}C \rangle$  when B<sub>2</sub>O<sub>3</sub> is in the batch in a high degree still free and occurs in the amorphous and liquid phase respectively. The water steam content in the tablet increases due to the dehydroxidation of kaolinite (illite). At the temperatures above  $600 \text{ }^\circ\text{C}$  the B<sub>2</sub>O<sub>3</sub> loss rate from the pressed batch decreases to a non-zero value because water steam probably reacts even with the produced borates (particularly with the magnesium and calcium borates).

The temperature dependence of  $B_2O_3$  loss from the modified Eutal glass batch containing 7.51 mass % of calcite and 7.51 mass % of calcium hydroxide is drawn on curve *d* in Fig. 4. (column d in Table II). The  $B_2O_3$  loss increases due to the decomposition of Ca(OH)<sub>2</sub> in the temperature range of  $\langle 300 \, ^\circ C, 500 \, ^\circ C \rangle$ .

Between 500 °C and 700 °C the losses of  $B_2O_3$  from the original and modified batch are approximately equal. Regarding the primary  $B_2O_3$  content the total  $B_2O_3$  loss in the modified batch, however, is higher than in the original batch  $(100 \cdot m_g(B_2O_3)/m_0(B_2O_3) \approx 17.4 \%)$ . A supposed decrease of  $B_2O_3$  loss from (100  $m_g(B_2O_3)/m_0(B_2O_3) \approx 17.4 \%)$ . A supposed decrease of  $B_2O_3$  loss from the mo-



Fig. 5. The content of B<sub>2</sub>O<sub>3</sub> in the pressed samples of system of H<sub>3</sub>BO<sub>3</sub>-kaolin, heated in the gas mixture of composition as 80 vol. % N<sub>2</sub>, 20 vol. % H<sub>2</sub>O versus temperature

- a) the curve of content of chemically bounded  $B_2O_3$ ,
- b) the curve of free  $B_2O_3$ ,
- c) the B<sub>2</sub>O<sub>3</sub> loss due to reactive vaporization from pressings to environs.

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dified batch was not observed even though calcium borates, proved by the phase analysis, were generated already in the lower temperature range.

Mass balance results of condensed and gaseous phase of  $B_2O_3$  for the pressings of the kaolin—boric acid binary model system are presented in Fig. 5. From shape of the curve of the bound  $B_2O_3$  content (curve a) and that of the free  $B_2O_3$  content (curve b) versus temperature it follows that the both components and the products of their decomposition react mutually in the whole observed temperature range of  $\langle 450 \, ^\circ C, \, 800 \, ^\circ C \rangle$ , where dehydratation of kaolinite and illite (admixture in kaolin) respectively was observed. Products of these reactions are aluminium borates. As it has been proved 9 Al<sub>2</sub>O<sub>3</sub> · 2 B<sub>2</sub>O<sub>3</sub> was primarily generated and 2 Al<sub>2</sub>O<sub>3</sub> · B<sub>2</sub>O<sub>3</sub> was produced to a lower extent.

The  $B_2O_3$  loss values in the range of  $\langle 450 \text{ °C}, 800 \text{ °C} \rangle$  for the studied binary system are arrayed also in column e in Table II. The experimental data dispersion is probably due to imperfection of the used method described above.

#### 4. CONCLUSION

From the all presented results of measurements it follows that in the process of heating the batch in the stream of natural gas combustion products the loss of  $B_2O_3$  is two times higher in comparison with that when the batch is heated in waterless gaseous stream. The total  $B_2O_3$  loss related to the primary content of  $B_2O_3$  in the batch  $(100 \cdot m_g(B_2O_3)/m_0(B_2O_3)) \approx 14.5\%)$ , after the heating up

#### Table III

The mass balance of the gaseous reaction products loss in the process of pressed Eutal glass batch heating.

a) Heating in the mixture of 70 vol. % of N<sub>2</sub>, 20 vol. % of H<sub>2</sub>O, 10 vol. %

of CO<sub>2</sub>. b) Heating in N<sub>2</sub>

Product	$-\frac{m_{\rm g}(i)}{m_0} /\%$							
ℓ/°C		<b>2</b> 00	300	400	500	600	700	800
H2O (humidity)	a) b}	<b>3.</b> 0 <b>3</b> .0	3.0 3.0	3.0 3.0	3.0 3.0	3.0 3.0	3.0 3.0	<b>3</b> .0 <b>3</b> .0
H2O (H3BO3)	a) b)	4.4 4.3	4.9 4.9	5.1 4.9	4.8 4.9	4.8 5.0	4.8 5.1	4.6 5.1
H₂O (kaolín)	a) b)				1.1	2.7 2.3	3.6 3.6	3.6 3.6
CO <sub>2</sub> (calcite)	a) b)	0.3 0.2	1.0 0.4	1.1 0.4	1.4 0.4	1.4 0.5	2.8 1.4	2.8 1.4
CO2 (dolomite)	a) b)			Ē		. ·		5.4 4.0
H <sub>3</sub> BO <sub>3</sub> (g)	a) b)	0. <b>3</b> 0.5	0.4 0.5	1.0 0.7	1.6 1.0	1.6 0.9	1.6 0.8	1.8 0.8
$\frac{1}{m_0}\sum_i m_{\rm g}(i)$	a)	7.9	9.5	10. <b>2</b>	11.8	13.4	15.7	21.3
-	b)	7.9	7.8	8.4	9.3	12.4	14.8	19.1

of the pressed Eutal glass batch to 800 °C is obviously not a finite value even though after heating almost all boric oxide is bounded in form of borates. The  $B_2O_3$  leakage was higher due to  $Ca(OH)_2$  that partially replaced calcite.

The mass balance of all gaseous products generated in the process of heating the Eutal glass batch in the combustion products gas stream or in nitrogen stream is presented in Table III. Higher decrease of  $CO_2$  and  $H_2O$  mass in the combustion products atmosphere within the whole temperature range reffers accelerating influence of water steam on decomposition of calcite and dolomite and on reactivity among the batch components.

The presented data were a basis for investigation of reaction mechanism in the process of heating of the pressed Eutal glass batch up to 800  $^{\circ}$ C in the combustion products atmosphere and for determination of enthalpy balance of this process. Results of this exploration are presented in part two.

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## BILANCIA CHEMICKÝCH, FÁZOVÝCH A ENTALPICKÝCH ZMIEN V PRIEDHRIEVANOM LISOVANOM KMENI PRE SKLO EUTAL I.

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Cieľom tejto práce bolo určenie hmotnostnej bilancie úniku plynných reakčných produktov (CO<sub>2</sub>(g), H<sub>2</sub>O(g) a plynných foriem kyseliny boritej (HBO<sub>2</sub>(g), H<sub>3</sub>BO<sub>3</sub>(g)) počas záhrevu lisovaného kmeňa pre sklo Eutal v teplotnom intervale  $\langle 25 \, ^{\circ}C, 800 \, ^{\circ}C \rangle$  v prúde plynnej zmesi približného zloženia spalín, odchádzajúcich zo sklárskych taviacich agregátov (70 % N<sub>2</sub>, 20 % H<sub>2</sub>O, 10 % CO<sub>2</sub>), alebo v prúde čistého dusíka. Vzorky lisovaného kmeňa v tvare valčekov s hmotnosťou asi 2 g sa zahrievali rýchlosťou vzrastu teploty 10 °C . min<sup>-1</sup> vo vodorovnej piecke v prúde plynov voliteľného zloženia. Zo zahrievaných výliskov unikali plynné reakčné produkty (kyselina boritá, vodná para a oxid uhličitý), hmotnosti ktorých  $m_g(X)$  sa kvantitatívne stanovovali kombináciou metód termogravimetrickej, chemickej a atómovej spektrálnej analýzy.

Plynná kyselina boritá sa tvorila počas záhrevu výlisku reakciou oxidu boritého prítomného v kmeni s vodnou parou, ktorá vzniká v kmeni odparením vlhkosti, termickým rozkladom surovín, obsahujúcich štruktúrne viazanú vodu (v teplotnom rozmedzí asi 120-250 °C prebieha rozklad H<sub>3</sub>BO<sub>3</sub> a v rozmedzí asi 450-700 °C prebieha dehydroxidácia kaolínu) a je tiež zložkou spalín. Pri záhrevoch výliskov kmeňa Eutal v prúde dusíka, kedy se z kmeňa uvolní vodná para s hmotnosťou asi 11,8% z počiatočnej hmotnosti kmeňa, je celková strata B<sub>2</sub>O<sub>3</sub> asi 7% z jeho počiatočného obsahu v kmeni. Pri záhrevoch v prúde spalín za inak rovnakých podmienok je celková strata B<sub>2</sub>O<sub>3</sub> približne dvojnásobná – jej hodnota je 14,5% vzhľadom na počiatočný obsah B<sub>2</sub>O<sub>3</sub> v kmeni.

Hmotnosti ovidu uhličitého a vodnej pary, ktoré unikli zo zahrievaného kmeňa počas záhrevu, sa stanovovali:

a) u záhrevov výliskov kmeňa Eutal v prúde dusíka sa  $CO_2(g)$  absorboval do  $Ba(OH)_2$  a jeho obsah sa stanovil rozpustením  $BaCO_3$  v HCl a titráciou prebytočrej kyseliny roztokom NaOH.  $H_2O(g)$  sa získala odčítaním súčtu  $m_g(H_3BO_3)$  a  $m_g(CO_2)$  od celkového úbytku hmotnosti zahriateho výlisku;

b) u záhrevov výliskov kmeňa Eutal v prúde spalín sa hodnoty  $m_g(CO_2)$  a  $m_g(H_2O)$  vypočí-

tali na základe známeho zloženia kmeňa pre sklo Eutal (Tab. I) a s použitím hmotnostných zlomkov oxidu uhličitého a vody v ochladených predohriatych výliskoca, určených TG-analýzou.

Vyššie úbytky všetkých plynných reakčných produktov pri záhrevoch výliskov kmeňa Eutal v atmosfére spalín v celom sledovanom teplotnom rozmedzí ukazujú na urychľujúci vplyv vodnej pary na chemické reakcie, prebiehajúce v zahrievanom kmeni.

- Obr. 1. Laboratórne zariadenie pre záhrevy výliskov kmeňa pre sklo Eutal a subsystémy v kontrolovatelnej atmosfére prúdiacich plynov naprogramovateľnými rýchlosťami vzrastu teploty.
- Obr. 2. Sústava TG-kriviek lisovaného kmeňa pre sklo Eutal, predhrievaného v atmosfére plynov zloženia spalín zemného plynu v intervaloch 25 °C t; t  $\in \langle 200 \text{ °C} \rangle$ .
- Obr. 3. Sústava DTA-kriviek lisovaného kmeňa pre sklo Eutal, predhrievaného v atmosfére plynov zloženia spalín zemného plynu v intervaloch 25 °C t; t  $\in \langle 200 \text{ °C} \rangle$ .
- Obr. 4. Grafické závislosti relatívnej straty oxidu boritého od teploty z lisovaného kmeňa pre sklo Eutal, zahrievaného v prúde plynov pri rýchlosti rastu teploty 10 °C : min-1
  - a) závislosť pre lisovaný kmeň priemyseľného zloženia pre sklo Eutal (tab. I), zahrievaný v prúde spalín zemného plynu,
  - b) závislosť pre lisovaný kmeň rovnakých vlastností ako v prípade a), zahrievaný v prúde  $N_{2,*}$
  - c) výsledky práce [4],
  - d) závislosť pre lisovaný kmeň s modifikovaným zložením (obsahuje 7,51% vápenca a 7,51% Ca(OH)2).
- Obr. 5. Teplotné závislosti obsahu B<sub>2</sub>O<sub>3</sub> vo výliskoch sústavy kyselina boritá-kaolín, zahrievaných v prúde plynnej zmesi zloženia 80 obj. % N<sub>2</sub>, 20 obj. % H<sub>2</sub>O:
  - a) závislosť B<sub>2</sub>O<sub>3</sub> chemicky viazaného vo forme boritanov v kondenzovanej fáze,
  - b) závislosť volného B2O3 v kondenzovanej fáze,
  - c) závislosť straty B<sub>2</sub>O<sub>3</sub> reaktívnym prchaním z výliskov do okolia.

# МАТЕРИАЛЬНЫЙ БАЛАНС ХИМИЧЕСКИХ, ФАЗОВЫХ И ЭНТАЛЬПИЧЕСКИХ ПРЕВРАЩЕНИЙ В ПОДОГРЕВАЕМОЙ ОТПРЕССОВАННОЙ СТЕКЛОМАССЕ, ПРЕДНАЗНАЧЕННОЙ ДЛЯ СТЕКЛА Eutal. I.

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Целью предлагаемой работы является установление материального баланса утечки газообразных реакционных продуктов (CO<sub>2</sub> (г), H<sub>2</sub>O (г)) и газообразных форм борной кислоты (HBO<sub>2</sub> (1), H<sub>3</sub>BO<sub>3</sub> (г)) во время нагрева отпрессованной стекломассы, предназначенной для стекла Eutal в температурной интервале < 25 °C, 800 °C > в потоке газообразных агретатов (70 % N<sub>2</sub>, 20 % H<sub>2</sub>O, 10 % CO<sub>2</sub>), или в потоке чистого азота. Пробы отпрессованной стекломассы в виде роликов весом приблизительных оставом составом продуктов сгорания, уходящих из стекловаренных агретатов (70 % N<sub>2</sub>, 20 % H<sub>2</sub>O, 10 % CO<sub>2</sub>), или в потоке чистого азота. Пробы отпрессованной стекломассы в виде роликов весом приблизительно 2 г нагревали скоростью роста температуры 10 °C. мин<sup>-1</sup> в горизонтальной печке в потоке газообразные реакционные продукты (борная кислота, водяной пар и двуокись углерода), вес которых  $m_r(X)$  количественно устанавливали, комбинируя методы термогравиметрического, химического и атомного спектрального анализа.

Газообразная борная кислота образуется во время нагревания отпрессованного изделия взаимодействием оксида трехвалентного бора, содержащегося в стекломассе, с водяным паром, образующимся в стекломассе испарением влажности, термическим разложением сырья, в состав которого входит структурно связанная вода (в температурном пределе приблизительно 120—250 °С протекает разложение H<sub>3</sub>BO<sub>3</sub> и в пределах приблизительно 450—700 °С протекает дегидроксидация каолина), которая является также составной частью продуктов сгорания. При нагревах отпрессованных изделий стекломассы Eutal в потоке язота, когда из стекломассы выделяется водяной пар весом

приблизительно 11,8 % при пересчете на исходный вес стекломассы, общие потери В<sub>2</sub>О<sub>2</sub> составляют приблизительно 7 % при пересчете на его исходный вес в стекломассе. При нагревах в потоке продуктов сгорания при одинаковых условиях общие потери В2О3 приблизительно в два раза выше — они достигают величины 14,5 % при пересчете на исходное содержание B<sub>2</sub>O<sub>3</sub> в стекломассе.

Вес двуокиси углерода и водяного пара, утекающих из нагреваемой стекломассы во время нагрева. устанавливали:

а) у нагрева отпрессованных изделий стекломассы Eutal в потоке азота CO<sub>2</sub> (г) абсорбировал в Ва(OH)<sub>2</sub> растворением ВаСО<sub>3</sub> в HCl и титрованием избыточной кислоты раствором NaOH.  $H_2O(r)$  получали отсчетом суммы  $m_r(H_3BO_3)$  и  $m_r(CO_2)$  от общих. потерь в весе нагреваемого отпрессованного изделия.

б) у нагрева отпрессованных изделий стекломассы Eutal в потоке продуктов сгорания величины m<sub>1</sub>(CO<sub>2</sub>) и m<sub>1</sub>(H<sub>2</sub>O) расчитывали на основе известного состава стекломассы для стекла Eutal (табл. I) и с применением весовых дробей двуокиси углерода и воды в охлажденных подогреваемых отпрессованных изделиях, установленных с помощью TG-анализа.

Более высокие потери всех газообразных реакционных продуктов при нагреве отпрессованных изделий стекломассы Eutal в среде продуктов сгорания в общих исследуемых пределах температуры являются свидетельством ускоряющегося влияния водяного пара на химические реакции, протекающие в нагреваемой стекломассе.

- Рис. 1. Лабораторная установка для нагрева отпрессованных изделий стекломассы, предназначенной для стекла Eutal и подсистемы в контролируемой среде протекающих газов запрограммируемыми скоростями роста температуры.
- Рис. 2. Система TG-кривых отпрессованной стекломассы для стекла Eutal, подогреваемого в среде газов составом продуктов сгорания природного газа в интервалах 25 °C -t;  $t \in \langle 200 \ ^{\circ}C, 800 \ ^{\circ}C \rangle$ .
- Рис. 3. Система DTA-кривых отпрессованной стекломассы для стекла Eutal, подогрезаемого в среде газов составом продукров сгорания природного газа в интервалах  $25 \ ^{\circ}C - t$ ;  $t \in \langle 200 \ ^{\circ}C, 800 \ ^{\circ}C \rangle$ .

Рис. 4. Графические зависимости относительной потери оксида трехвалентного бора от температуры из отпрессованной стекломассы для стекла Eutal. нагреваемого е потоке газов при скорости роста температуры 10 °C. мин<sup>-1</sup>:

а) зависимость для отпрессованной стекломассы промышленного сотсава для стекла Eutal (табл. I), нагреваемой в потоке продуктов сгорания природного газа.

6) зависимость для отпрессованной стекломассы одинаковых свойств как в случае

- а), нагреваемой в потоке N<sub>2</sub>,

в) результаты работы [4], г) зависимость для отпрессованной стекломассы модифицированного соста**ва** (содержащего 7,51 % известняка и 7,51 % Ca(OH)2).

Рис. 5. Температурные зависимости содержания В2О3 в отпрессованных изделиях системы борная кислота—каолин, нагреваемых в потоке газообразной смеси составом 80 % по весу N<sub>2</sub>, 20 % по весу H<sub>2</sub>O:

а) зависимость B2O3 химически связанного в виде боратов в конденсированной фаге,

б) зависимость свободного B2O3 в конденсированной фазе,

в) зависимость потери B2O3, вызванной относительным улетучиванием из отпрессованных игделий в среду.