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

II. Determination of phase and enthalpy changes

Mária Eliášová,* Milan Košecký, Mária Rekeńová, Ivo Proks

Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská 5, 842 36 Bratislava *Institue of Glass Research and Development,

SNP street 20, 912 50 Trenčin

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A quantitative description of chemical processes and enthalpy changes in the pressed Eutal glass batch of 3-4% initial humidity that was heated in the stream of natural gas combustion products in the range of $\langle 25 \,^{\circ}C \,^{\circ}S0 \,^{\circ}C \rangle$ is presented in this paper. During heating water is released from H_3BO_3 and kaolin and approximately 67 % of CO_2 escape from dolomite and calcite by thermic decomposition. Interaction among components gradually generates calcium borates (primarily CaO $\cdot B_2O_3$, 2 CaO $\cdot 3 B_2O_3$, 2 CaO $\cdot B_2O_3$), aluminium borates (9 $Al_2O_3 \cdot 2 B_2O_3$, 2 $Al_2O_3 \cdot B_2O_3$), 2 MgO $\cdot B_2O_3$, CaO $\cdot 2 Al_2O_3$, MgO, CaO, etc. Transition of B_2O_3 to the bound state (at 800 $^{\circ}C$ free B_2O_3 is not present in the batch) decreases B_2O_3 leakage from the batch that is caused by reactive escaping in water steam. A total heat consumption for heating the batch and for reactions in it was estimated as $\Delta h (\langle 25 \,^{\circ}C, 800 \,^{\circ}C \rangle) = 1630 - 1670 \, kJ \cdot kg^{-1}$.

1. INTRODUCTION

In the second part of this paper a quantitative description of chemical processes and enthalpy changes in the pressed Eutal glass batch gradually heated from 25 °C to 800 °C in a stream of an approximate composition of natural gaseous products is presented. A phase and enthalpy analysis has been worked out on the basis of the mass balance of the gases escaping from batch owing to chemical reactions and thermic decomposition of some batch components in the process of heating the batch. Further methods were used also (above all X-ray, DTA and DSC analyses). Results of the mass balance of the gaseous products escaping from the batch in the range of 25 °C to 800 °C are presented in the first part of the paper.

On the one hand the aim of the following exploration of chemical processes and enthalpy changes in the process of heating the Eutal batch was to consider the possibility of using the combustion product enthalpy for pre-heating a batch charge before its insertion into the melting aggregate. It was, on the other hand, a chemical evaluation of the process in the heated batch and its relation to an escape of B_2O_3 from the batch as a consequence of a reaction with water steam (reactive evaporation).

The composition of the batch for the Eutal glass is in Table I (column 1). This is a classical batch composition for Eutal glass production at the fy Skloplast in Trnava. A component giving B_2O_3 is the trihydrogenboric acid H_3BO_3 , a syntetic raw-material that besides having other advantages, is of a high degree of purity, that guarrantees homogenity of the produced glass. A disadvantage in it, however, is that structurally bound water that is released takes along with it molecules

of H_3BO_3 and HBO_2 in a gaseous phase. An escape of B_2O_3 from batch makes kaolin also disadvantageous because it releases water by thermal decomposition in the temperature range of 450 C to 700 °C. From this point of view it is necessary to explore the possibilities of how the raw-material composition of the Eutal glass batch could advantageously be modified by some other technically available compounds, that would contain CaO, MgO, or Al₂O₃, to increase within the given temperature range the reaction intensity of these compounds with H_3BO_3 producing borates and thus decreasing the free B_2O_3 content.

2. CHEMICAL REACTIONS IN THE PRESSED EUTAL GLASS BATCH WITHIN THE RANGE OF 25 °C TO 800 °C

The most reactive components of the observed composition batch for the Eutal glass are H_3BO_3 and its dehydratation products (HBO_2 , B_2O_3). Already at room temperature H_3BO_3 reacts with CaCO₃ in the batch. The reaction produces hydrates of calcium borates with a considerable prevalence of the CaO. $3 B_2O_3$. $4 H_2O$ phase. The batch stored in a closed place for a few days (about 6) has its H_3BO_3 already reacted off.

The water that is released from the reaction makes the batch grow damp, increasing volume so that the batch tablets are deformed and begin to fall apart. In the following report we present the reactions that were gradually in process in the heated batch just after its pressing under the conditions presented in the first part of this paper. The values of the specific reaction enthalpies Δh_r , that are valid for 1 kg of the glass batch, were computed with the use of tables [1, 2] on the basis of the phase analysis of the samples heated in the given temperature range. Some of estimates of the Δh_r values were also estimated by direct measurement of the reaction heat in the DSC calorimeter in the temperature range of 25 °C to 700 °C.

 H_2O (l) evaporates at 100 °C. The humidity of the batch is 3—4 mass % (that is the natural humidity and the additional humidity for making the batch easily pressable).

The water evaporation can be described by the following scheme:

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta h_r = 70 - 95 \text{ kJ} \cdot \text{kg}^{-1}.$$
 (1)

The H_3BO_3 decomposes into boric oxide B_2O_3 in about 120–250 °C range. This process can be described by the following equations [3]:

$$H_3BO_3 \rightarrow HBO_2 + H_2O \qquad \Delta t = 120 - 170 \,^{\circ}C,$$
 (2)

$$2 H_3 BO_3 (s) \rightarrow 1.16 HBO_2 (s) + 2.42 H_2 O (g) + 0.42 B_2 O_3 (am) t = 170 °C, (3)$$

HBO₂ (s)
$$\rightarrow 0.5 \text{ B}_2\text{O}_3 \text{ (am)} + 0.5 \text{ H}_2\text{O} \text{ (g)} \qquad \Delta t = 170 - 250 \text{ °C.} \quad (4)$$

The sum of the reaction enthalpies is $\Delta h_r \approx 160 \text{ kJ}$. kg⁻¹.

Both forms of boric acid and the produced B_2O_3 react in a low degree with the original CaCO₃ generating calcium borates in the range of 25 °C to 400 °C. With regard to a content of water in the system there are hydrates of calcium borates that may lose their hydrate water primarily in the range of 300 °C to 400 °C.

In a simplified way the origin of calcium borates at 300 °C can be described as follows:

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$$14 \text{ HBO}_2 + 4 \text{ CaCO}_3 \rightarrow \text{ CaO} \cdot \text{B}_2\text{O}_3 \cdot x\text{H}_2\text{O} + \text{CaO} \cdot 3 \text{B}_2\text{O}_3 \cdot y\text{H}_2\text{O} + + 2 \text{ CaO} \cdot 3 \text{B}_2\text{O}_3 \cdot z\text{H}_2\text{O} + 4 \text{ CO}_2 + (7-x-y-z)\text{H}_2\text{O}.$$
(5)

The numbers of the crystal water molecules x = 2, y = 1, z = 1 were taken on the basis of the TG curves analysis at 200 °C. From the shape of the TG and DTA curves [Fig. 2., 3., paper 1] one can presume that the dehydratation of calcium borates runs up to 400 °C. The total sum Δh_r of the reaction enthalpies concerned with the origin of hydrates of calcium borates and their dehydratation is estimated to be 50 kJ. kg⁻¹. From X-ray analysis of samples of pre-heated binary system lime-stone-H₃BO₃ and of Eutal glass batch, stored the same time at 25 °C and than heated, it follows, that the CaO. 3 B₂O₃. xH_2O component reacts with CaCO₃ from about 200 °C producing CaO. B₂O₃. nH_2O and 2 CaO. 3 B₂O₃.

Within the whole temperature range $\langle 25 \, ^\circ C, 800 \, ^\circ C \rangle$ the condensed boric oxide B_2O_3 reacts with water steam generating gaseous compounds H_3BO_3 (g) and HBO_2 (g) or an escape of the condensed boric acid out of the batch takes place (look at the first part of the paper).

The total reaction enthalpy value Δh_r concerned with the transition of H₃BO₃ (s), HBO₂ (s) and B₂O₃ (cond.) into the gaseous forms of boric acid in the $\langle 25 \,^{\circ}\text{C}, 800 \,^{\circ}\text{C} \rangle$ range was estimated to be 118 kJ . kg⁻¹.

Boric oxide melts at 450 °C and the dehydratation of kaolinite (illite) that is present in the system starts approximately at the same temperature by the following equations:

 $Al_2O_3 \cdot 2 SiO_2 \cdot 2 H_2O \rightarrow Al_2O_3 \cdot 2 SiO_2 + 2 H_2O \Delta h_r \approx 325 \text{ kJ} \cdot \text{kg}^{-1}$. (6)

The originating metakaolinite Al_2O_3 . 2 SiO₂ reacts with B_2O_3 (l) producing aluminium borates 9 Al_2O_3 . 2 B_2O_3 and 2 Al_2O_3 . B_2O_3 as the following approximate scheme describes:

 $11 (Al_2O_3 \cdot 2 \operatorname{SiO}_2) + 3 B_2O_3 \rightarrow 9 Al_2O_3 \cdot 2 B_2O_3 + 2 Al_2O_3 \cdot B_2O_3 + 22 \operatorname{SiO}_2. (7)$

The contents of the both reaction products in the $\langle 600 \text{ °C}, 800 \text{ °C} \rangle$ range were determined:

a) on the basis of the quantitative phase analysis results in the system kaolinite - H₃BO₃ that was heated under almost the same conditions as the complete batch;

b) by using the value of the total reaction heat measured in the DSC calorimeter $\Delta h_{\rm r} = 160-170 \ {\rm kJ} \cdot {\rm kg}^{-1}$. This value is different from the expected value of enthalpy 320-330 kJ · kg⁻¹ describing the decomposition of kaolinite present in the system. The difference between the both values of $\Delta h_{\rm r}$, equal to -160 kJ . kg⁻¹ is due to exothermic reaction, in the range of 500 °C to 600 °C (above all to origination of both aluminium borates.). Their mass in the system was calculated with the use of stechiometry owing to knowledge of mass fraction of decomposed kaolin;

c) by supposing that B_2O_3 tends to generate both aluminium borates to the same extent. On this assumption the content of $9 Al_2O_3 \cdot 2 B_2O_3$ is two times higher than of $2 Al_2O_3 \cdot B_2O_3$ in the batch which is proved by X-ray analysis of both phases in the observed systems. The total reaction enthalpy concerned with the originating of $9 Al_2O_3 \cdot 2 B_2O_3$ and $2 Al_2O_3 \cdot B_2O_3$ in the $\langle 500 \, ^\circ C, 700 \, ^\circ C \rangle$ range is estimated to be $\Delta h_r = (-110)-(-120) \text{ kJ} \cdot \text{kg}^{-1}$.

In the $\langle 600 \,^{\circ}C \rangle$ range the mass fraction of carbon dioxide CO₂, released as a consequence of a reaction CaCO₃ with B₂O₃, increased from 1.4 mass % to 2.8 mass %. Because the mass fraction w(CaO) (in undecomposed calcium carbo-

nate)/ $w(B_2O_3)$ at 600 °C is approximately 2 : 1, the further generating of 2 CaO. . B_2O_3 with the increase of temperature can be supposed as this scheme describes:

$$2 \operatorname{CaCO}_3 + \operatorname{B}_2 \operatorname{O}_3 \rightarrow 2 \operatorname{CaO} \cdot \operatorname{B}_2 \operatorname{O}_3 + 2 \operatorname{CO}_2$$

$$\Delta h_r \approx 15 \text{ kJ} \cdot \text{kg}^{-1} \quad \text{for } \Delta t = 600 - 700 \text{ °C}.$$
(8)

 \mathbb{X} A presence of 2 CaO . B₂O₃ in the system at 700 °C and 800 °C was proven by X-ray analysis. The generating of 2 CaO . B₂O₃ also follows from the shape of the DTA curves.

Dolomite that didn't reacted in lower temperatures starts to disintegrate thermally at 700 °C according to the scheme:

$$CaCO_3 \cdot MgCO_3 \rightarrow CaCO_3 + MgO + CO_2 \qquad \Delta h_r \approx 79 \text{ kJ} \cdot \text{kg}^{-1}.$$
 (9)

 $CaCO_3$ produced in the reaction reacts first with the rest of B_2O_3 and $Al_2O_3 \cdot 2 \operatorname{SiO}_2$ and to a low extent with SiO_2 (X-ray analysis of the experimental tablets heated at 800 °C proved the presence of 2 CaO. SiO₂ and 2 MgO. SiO₂).

The products of decomposed dolomite react with boric oxide B_2O_3 as follows:

$$2 \operatorname{CaCO}_3 + B_2 O_3 \rightarrow 2 \operatorname{CaO} \cdot B_2 O_3, \qquad (10)$$



Fig. 1. The mass balance of B₂O₃ in the pressed Eutal glass batch heated in the stream of natural gas combustion products

a) the content of free B_2O_3 versus temperature, b) the content of bounded B_2O_3 versus temperature, c) the B_2O_3 loss from pressed batch versus temperature. respectively

$$CaCO_3 + CaO \cdot B_2O_3 \rightarrow 2 CaO \cdot B_2O_3 + CO_2 \qquad \Delta h_T \approx 12 \text{ kJ} \cdot \text{kg}^{-1}$$
 (11)

and

$$2 \text{ MgO} + B_2 O_3 \rightarrow 2 \text{ MgO} \cdot B_2 O_3 \qquad \Delta h_r \approx -3 \text{ kJ} \cdot \text{kg}^{-1}.$$
 (12)

From the shape of the TG and DTA curves (first part of the paper, Fig. 2; 3) it follows that the free B_2O_3 (cond.) is present in the batch up to approximately 750 °C. In the observed temperature range $\langle 25 \, ^\circ C, 800 \, ^\circ C \rangle$ all boric oxide passes to a bound state in the form of calcium, aluminium and magnesium borates. A beneficial result of dissapearing of the free B_2O_3 from the system is an expected decrease or a total suppression of B_2O_3 escape with the further temperature increase (first part of the paper, Fig. 4, curve a — the tablets were heated in the combustion products; curve b — the tablets were heated in pure N_2). A certain loss of B_2O_3 is observed in the range between 700 °C and 800 °C (part one, Fig. 4., curve a). The loss is probably due to the hydrolysis of borates in the moist combustion product atmosphere.

In Fig. 1, curve a and b illustrate the graphical dependence of the content of free B_2O_3 versus temperature and of the content of bound B_2O_3 versus temperature respectively. Curve c illustrates the temperature dependence of the loss of B_2O_3 by reactive escaping from the batch. From X-ray analysis they have found that metakaolinite Al_2O_3 . 2 SiO₂ reacts with CaCO₃ above 600 °C generating CaO. 2 Al_2O_3 as the following equation describes:

$$\begin{aligned} \operatorname{CaCO}_3 + 2 & (\operatorname{Al}_2\operatorname{O}_3 \cdot 2\operatorname{SiO}_2) & \rightarrow & \operatorname{CaO} \cdot 2\operatorname{Al}_2\operatorname{O}_3 + 4\operatorname{SiO}_2 + \operatorname{CO}_2 & (13) \\ \Delta h_r &\approx -50 \text{ kJ} \cdot \text{kg}^{-1} & \text{for } \Delta t = 600 - 800 \text{ °C.} \end{aligned}$$

The loss of CO₂ at 800 °C proves that about 90 % of dolomite decomposed under the given conditions. Between 700 °C and 800 °C CaO is also produced by the thermic decomposition of CaCO₃ (produced through the decomposition of dolomite)

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \Delta h_r \approx 57 \text{ kJ} \cdot \text{kg}^{-1}.$$
 (14)

3. PHASE ANALYSIS AND ENTHALPY BALANCE OF THE PROCESS IN THE PRESSED BATCH IN THE TEMPERATURE RANGE OF 25 °C TO 800 °C

Using the results which ensued from the analyses described in the first part of the paper, probable mass fraction values of the compounds present in the heated system were estimated. A total quantitative phase analysis of the pressed Eutal batch in the range of $\langle 25 \, ^{\circ}C \rangle$ is presented in Table I.

A total enthalpy balance of the process during the heating of the pressed batch for the Eutal glass in the temperature range of $\langle 25 \, ^{\circ}C, 800 \, ^{\circ}C \rangle$ is given in the Table II. The calculations were done using the enthalpies of formation of batch components and reaction products from thermodynamic tables [1] and [2] and were supported by the values of the calorimetric measured reaction enthalpies concerned with the reaction in the heated Eutal batch and its subsystems. The total amount of enthalpy of the batch heated in temperature intervals of 25 °C was figured out from the reaction scheme

$$\Delta h(\langle 25 \, ^{\circ}\mathrm{C}, t \rangle) = \sum_{i} m_{i}(t) \cdot h_{f}(i, \mathrm{pr}, t) - \sum_{j} m_{j}(25 \, ^{\circ}\mathrm{C}) \cdot h_{f}(j, \mathrm{r}, 25 \, ^{\circ}\mathrm{C}); \qquad (15)$$

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i, pr is the i-th product component of the heated batch;

j, r is the j-th component of the original batch;

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 $m_{i,(j)}$ is the mass of the *i*-th (*j*-th) component in 1 kg of the batch;

 $h_i(i(j) t)$ is the enthalpy of formation of the i(j)-th component.

A total consumption of enthalpy $(\Delta h (\langle 25 \text{ °C}, 800 \text{ °C} \rangle) = 1630-1670 \text{ kJ} \cdot \text{kg}^{-1})$ for heating the Eutal batch up to 800 °C is approximately one half of the value 3350-3790 kJ $\cdot \text{kg}^{-1}$ that represents a theoretical consumption of melting heat of the Eutal glass batch [4].

Table I The quantitative phase analysis of the pressed Eutal glass batch that was heated between 25 °C and 800 °C

Raw-material	$(m(i, t)/m_0(t_0))/\%$							
ℓ/°C	2 5	200	300	400	500	600	700	800
Sand	23.7	23.7	23.7	23.7	23.7	23.7	23.7	23.7
Kaolin	30.7	30.7	30.7	30.7	22.7	8.0	4.1	4.1
Limestone	15.2	14.4	12.8	12.5	11.8	11.8	8.6	8.6
Dolomite	13.1	13.1	13.1	13.1	13.1	13.1	13.1	1.2
H ₃ BO ₃	12.2						1	
CaF ₂	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
N62804	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
H ₂ O(l)	≈ 3.0							
		1						

Reaction products	$\frac{m(i, t)}{m_0(t)} 1\%$							
۶/°C	200	300	400	500	600	700	800	
HBO ₁	2.8							
B ₂ O ₃	3.3	4.5	3.9	3.0	2.7	1.2		
$CaO : 3 B_2O_3 : H_2O$	0.5							
$CaO \cdot B_2O_3 \cdot 2 H_2O$	0.5							
$CaO \cdot B_2O_3 \cdot 0.5 H_2O$		1.6						
$CaO \cdot B_2O_3$			1.6	2.1	2.1	2.6	2.6	
$2 \text{ CaO} \cdot 3 \text{ B}_2 \text{ O}_3 \cdot \text{H}_2 \text{ O}$	0.6	2.1						
$2 \operatorname{CaO} \cdot 3 \operatorname{B}_2 \operatorname{O}_3$			2.2	2.5	2.5	2.5	2.5	
$2 \operatorname{CaO} \cdot \operatorname{B}_2 \operatorname{O}_3$						2.0	3.3	
$Al_2O_3 \cdot 2 SiO_2$				6.9	16.9	12.2	9.6	
9 Al ₂ O ₃ . 2 B ₂ O ₃					1.3	3.0	3.0	
$2 \operatorname{Al}_2 O_3 \cdot B_2 O_3$					0.5	1.5	2.0	
β-SiO ₂					1.8	5.8	7.2	
CaO . 2 Al ₂ O ₃						1.5	3.0	
$2 \text{ MgO} \cdot \text{B}_2\text{O}_3$							1.9	
CaO							2.1	
MgO							1.6	
H ₂ O for pressing	3	3	3	3	3	3	3	
H ₂ O from H ₃ BO ₃	4.4	4.9	5.1	4.8	4.8	4.8	4.6	
H ₂ O from kaolin				1.1	2.6	3.7	3.7	
CO ₂	0.3	1.0	1.1	1.4	1.4	2.8	8.1	
H ₃ BO ₃ (g)	0.3	0.4	0.9	1.6	1.6	1.6	1.8	
				1				

t/°C	200	300	400	500	600	700	800
$\frac{\sum_{i} \Delta h(i(\text{cond}))/(\text{kJ} \cdot \text{kg}^{-1})}{\sum_{i} \Delta h(i(\text{g}))/(\text{kJ} \cdot \text{kg}^{-1})}$	225	306	382	50 3	562	665	676
	25	46	69	100	142	192	271
$\sum_{i}^{i} \Delta h_{r}(i\langle 25 \text{ °C}, t \rangle)/(\text{kJ} \cdot \text{kg}^{-1}) \\ \Delta h(\langle 25 \text{ °C}, t \rangle)/(\text{kJ} \cdot \text{kg}^{-1})$	242	294	340	451	561	562	696
	492	646	791	1054	1 2 65	1419	16 43

 $\sum_{i} \Delta h(i(\text{cond}))$ $\sum_{i} \Delta h(i(\mathbf{g}))$

- the heat content of the *i*-th condensed component in 1 kg of the heated batch.

(i(g)) - the heat content increase of the *i*-th gaseous component that was generated as a reaction product in the heated batch.

 $\sum \Delta h_r(i\langle 25 \text{ °C}, t \rangle)$ — the total reaction enthalpy of 1 kg of the batch in the interval of ($\langle 25 \text{ °C}, t \rangle$).



Fig. 2. The enthalpy change of pressed Eutal glass batch heated within 25-800 °C

the total enthalpy change versus temperature, ○ - the change of heat content of system (without reaction enthalpy), □ - the results of paper [5].

In Fig. 2. the curve with the experimental data (the full circles) represents the temperature dependence of total theoretical heat consumption for heating of the pressed Eutal batch, and the curve denoted by the empty circles represents the one of the enthalpy change of the whole system (condensed and gaseous components and with exclusion of reaction heats) of the heated batch versus temperature. On the curve denoted by the empty squares there are three heat consumption values that are needed for heating 5 kg of the pressed batch by the natural gas combustion products. Considerably higher values of heat consumption in [5] can at first be explained by a high degree of reacting off in the batch during

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experimental heatings of particular tablets under the laboratory conditions, further by a higher degree of humidity of the tablets and by including all batch components (gaseous products also) in the enthalpy balance calculation.

4. CONCLUSION

From the given results it follows that pre-heating the glass batch of Eutal outside the melting aggregate using the combustion products is a real possibility of utilizing combustion products waste heat. The combustion products composition, however, brings disadvantages as follows: The content of water vapour about 20% evokes the increasing of evaporation of the free B_2O_3 in comparison with an anhydrous atmosphere. Furthermore a mechanical processing of the glass batch is necessary because the combustion products stream during heating would make dehomogenity in a loose batch. The moist atmosphere, however, accelerates the B_2O_3 transition to a bound state in the form of calcium, aluminium and magnesium borates. It also positively catalyzes further reactions between the batch components when condensed and gaseous product originate. A considerably high degree of the B_2O_3 leakage from the given composition batch during its heating in the combustion products stream can be decreased by replacing $CaCO_3$ with CaO that has a higher capability to react with the batch components than $CaCO_3$.

In case of technological use of the results that are presented in both parts of the paper, the generated boric oxide B_2O_3 (and also SO_x and N_xO_y oxides) will be captured in the pre-heating equipment.

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BILANCIA CHEMICKÝCH, FÁZOVÝCH A ENTALPICKÝCH ZMIEN V PREDHRIEVANOM LISOVANOM KMENI PRE SKLO EUTAL. II.

Mária Eliášová, *Milan Košecký, Mária Rekeňová, Ivo Proks

Ústav anorganickej chémie SAV, Dúbravská 5, 842 36 Bratislava *Výskumný a vývojový ústav sklársky, tr. SNP 20, 912 50 Trenčín

Na základe výsledkov hmotnostnej bilancie plynných reakčných produktov a s použitím dalších analytických metód (rtg- a DSC-analýza, DTA, atómová spektrálna analýza) je vypracovaný kvantitatívny opis chemických dejov a entalpických zmien v lisovanom kmeni pre sklo Eutal, zahrievanom v prúde plynov zloženia spalín zemného plynu v intervale (25 °C, 800 °C) rýchlosťou zmeny teploty 10 °C. min⁻¹. Pri záhrevoch jednotlivých výliskov kmeňa Eutal v daných laboratórnych podmienkach sa termickým rozkladom uvoľnila prakticky všetka štruk-

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túrne viazaná voda z H₃BO₃ a z kaolínu a asi 67 % oxidu uhličitého CO₂(g) z dolomitu a vápenca Reakciami zložiek obsahujúcich bór s niektorými zložkami vznikajú v zahrievanom kmeni v celom teplotnom rozsahu boritany vápenaté, predovšetkým CaO. B₂O₃, 2 CaO. 3 B₂O₃, a 2 CaO. B₂O₃. Pri teplotách nad 500 °C vznikajú boritany hlinité 9 Al₂O₃. 2 B₂O₃ a 2 Al₂O₃. B₂O₃ a pri teplotách nad 700 °C sa tvoria fázy 2 MgO. B₂O₃, CaO. 2 Al₂O₃, MgO, CaO a i. Prechodom voľného B₂O₃ do viazanej formy sa znižujú jeho straty z kmeňa, vznikajúce reaktívnym prchaním účinkom vodnej pary. Odhad celkovej hodnoty prírastku entalpie, potrebnej na ohrev lisovaného kmeňa Eutal s 3 -4 % počiatočnou vlhkosťou a na reakcie prebiehajúce v ňom v rozmedzí 25-800 °C v daných podmienkach, Δh (<25 °C, 800 °C) = 1630-1670 kJ. kg⁻¹.

- Obr. 1. Hmotnostná bilancia B₂O₃ vo výliskoch kmeňa pre sklo Eutal zahrievaných v prúde spalín zemného plynu
 - a) graf teplotnej závislosti obsahu volného B₂O₃ vo výliskoch,
 - b) graf teplotnej závislosti B₂O₃ chemicky viazaného vo forme boritanov vo výliskoch,
 - c) graf teplotnej závislosti straty B2O3 do okolia výlisku.
- Obr. 2. Teplotná závislosť zmeny entalpie kmeňa pre sklo Eutal zahrievaného v rozmedzí 25-800 °C. ● - celková zmena entalpie, ○ - zmena tepelného obsahu sústavy (bez reakčnej entalpie)-

БАЛАНС ХИМИЧЕСКИХ, ФАЗОВЫХ И ЭНТАЛЬПИЧЕСКИХ ПРЕВРАЩЕНИЙ В ПОДОГРЕВАЕМОЙ ОТПРЕССОВАННОЙ СТЕКЛОМАССЕ, ПРЕДНАЗНАЧЕННОЙ ДЛЯ СТЕКЛА Eutal

Мария Элиашова, *Милан Кошецки, Мария Рекенева, Иво Прокс

Институт неорганической химии САН, Дубравска 5, 842 36 Братислава *Научно-исследовательский и проектный институт стекла, пр. СИР 20, 912 50 Тренчин

На осъовании результатов материальтого баланса газообразных продуктов реакция и с использованием дальнейших аналитических методов (rtg- и DSC-анализа, DTA, атомный спектральный анализ) разработали количественное описание химических процессов и энтальпических превращений в отпрессованной стекиомассе для стекла Eutal, нагреваемой в потоке газов составом продуктов сгорания природного газа в интервале <25°С, 800 °С) со скоростью изменения температуры 10 °С, мин-1. При нагревах отдельных отпрессованных изделий стекломассы Eutal в данных лабораторных условиях термическим распадом выделилась практически вся структурно- связанная вода из H₃BO₃ и из каолина и приблизительно 67 % двуокиси углерода CO₂ (г) из доломита и известняка. Реакциями компонентов, содержащих бор, с некоторыми составными частями образуются в нагреваемой стекломассе в целом температурном пределе бораты кальция, прежде всего CaO. B₂O₃, 2 CaO. 3 B₂O₃ р 2 CaO. B₂O₃. При температурах выше 500 °C образуются бораты алюминия 9 Al₂O₃. 2 B₂O₃ и 2 Al₂O₃. B₂O₃, а при температурах выше 700 °C образуются фазы 2 MgO. B₂O₃, CaO. 2 Al₂O₃, MgO, CaO и др. Переходом свободного B₂O₃ в связанную форму понижаются его нотери из стекиомассы, вызываемые реактивным улетучиванием под действием водяного пара. Предполагается общая величина прироста энтальнии, необходимой для нагрева отпрессованной стекломассы Eutal с 3—4 %-ой исходной влажностью и на реакции, которые в ней протекают в пределах 25—800 °С в данных усиовиях, $\Delta h (< 25$ °C, 800 °C >) = 1 630—1 670 кдж. . КГ⁻¹.

Рис. 1. Материальный баланс В2О3 в отпресованных изделиях стекломассы для стекла Eutal, нагреваемых в потоке продуктов сгорания природного газа:

а) график температурной зависимости содержания свободного B2O3 в отпрессованных изделиях,

б) график температурной зависимости B2O3, химически связанного в виде боратов в отпрессованных изделиях,

в) график температурной зависимости потерь B2O2 в близкую среду отпрессованного изделия.

 $[\]Box - v$ ysledky práce [5].

Рис. 2. Температурная гависимость изменения энтальпии стекломассы для стекла Eutal, нагреваемой в пределах 25—800 °C: ● — общее изменение энтальпии, О — изменение термического содержания системы (бег реакционной энтальпии), □ — результаты работы [5].