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USE OF DIFFERENT TYPES OF ALUMINUM-CONTAINING RAW MATERIALS IN TYPE-E FIBER PRODUCTION

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A comprehensive study was performed of various types of aluminum-containing raw materials and their effect on glass formation during smelting of borosilicate glasses for type-E fiber. It is shown that on use of non-metallurgical alumina, as compared with metallurgical alumina, disthene-sillimanite concentrate, and kaolin, a savings of energy resources for glass formation processes from 2.64 to 16.30% obtains.

Key words: borosilicate E-glass, continuous fiber, alumina, disthene-sillimanite concentrate, kaolin, glass formation, specific heat capacity, heat consumption, energy efficiency.

Increasing the efficiency of continuous fiber production is a multifactorial task. Among such factors the formulation of the chemical and charge composition of glasses is of great importance. In the production of continuous type-E electrical insulating fiber, glass compositions in accordance with ASTM D 578-00 are used, including (weight content, %): 52 – 62 SiO_2; 12 – 16 Al_2O_3; 0 – 10 B_2O_3; 16 – 25 CaO; 0 – 5 MgO; 0 – 2 $Na_2O + K_2O + Li_2O$; 0 – 1.5 TiO_2; 0.05 – 0.80 Fe_2O_3; 0 – 1 F^-.

In choosing energy-efficient compositions of type-E glasses it is necessary to make an assessment of their technological properties, such as crystallizability and temperature dependence of viscosity, which determine the technological parameters of fiber spinning [1]. A comprehensive study of type-E glasses revealed that boron-containing glass has technological advantages associated with more intense glass-making processes, and in terms of environmental performance the glass production process is comparable to the production of boron-free glass [2].

A judicious choice of raw materials, especially boron-containing raw materials, when making type-E glass affords an increase in the efficiency of glass-making processes [3, 4].

One of the main components of E-glass is alumina for which a number of raw materials are used in the charge. In the present work a comprehensive study was performed of the effect of various types of aluminum-containing raw materials on the glass-formation processes during glass melting for fiber. The objects of investigation are the following materials: metallurgical alumina (G-00 grade); non-metallurgical calcined alumina (White Alumina make); calcined disthene-sillimanite concentrate (disthene) (KDSP-K make); enriched kaolin (KZhF-1 make) (Table 1).

X-ray phase analysis (XPA) performed with a Bruker D8 Advance diffractometer showed the main crystalline phase for both types of alumina to be corundum α-Al_2O_3, whose content $\geq 90\%$. A feature of the phase composition of non-metallurgical alumina is the presence of γ-Al_2O_3, a more reactive modification of aluminum oxide, and gibbsite $Al(OH)_3$. The phase composition of the disthene-sillimanite concentrate is represented by sillimanite $Al_2O_3 \cdot SiO_2$ and impurity quartz.

Analysis of the particle-size distribution of the aluminum-containing raw materials was performed with an Analysette 22 MicroTec laser particle-size analyzer. The size of metallurgical alumina particles varies within wide limits — from 0.05 to 600 μm, and the content of particles larger than 150 μm is equal to 12.5%. Non-metallurgical alumina has a more uniform particle-size distribution and does not contain particles larger than 100 μm, the 20 – 50 μm fraction prevailing. In the granulometric composition of disthene, 10 – 70 μm particles make up 70% and > 100 μm particles 3%. Kaolin is distinguished by the highest dispersion among the investigated alumina-containing materials: the particle

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TABLE 1. Chemical Composition of Aluminum-containing Materials

Material	Weight content of the components, %									LOI
	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	ZrO_2	
Metallurgical alumina	0.02	98.80	–	–	0.14	0.02	0.03	–	–	1.0
Non-metallurgical alumina	0.01	98.57	–	–	0.16	0.01	0.05	–	–	1.2
Disthene	39.37	58.80	0.15	0.13	–	–	0.55	0.40	0.54	0.1
Kaolin	46.90	37.90	0.12	–	0.06	1.16	0.56	0.30	–	13.0

size does not exceed 50 μm, 5 – 20 μm particles comprise 57.5% and 0.05 – 5 μm — 39%.

The composition of type-E glass was picked to study the effect of the type of aluminum-containing raw materials on the glass-making processes (weight content, %): 53.0 SiO_2; 14.5 Al_2O_3; 9.0 B_2O_3; 20.0 CaO; 2.5 MgO; 0.5 Na_2O; 0.35 F^-; 0.15 Fe_2O_3. Four charge compositions were prepared using metallurgical alumina (composition 1), non-metallurgical alumina (composition 2), disthene (composition 3) and kaolin (composition 4).

The processes occurring during glass melting were studied by means of positional heat treatment of the charge performed in an electric furnace at temperatures from 900 to 1300 °C and soaking at the maximum temperature for 1 h.

At 1000°C the products of heat-treatment are a sintered body, the sample synthesized using non-metallurgical alumina having a denser structure. The higher dispersion of non-metallurgical alumina as compared with metallurgical alumina speeds up the silicate formation processes. The formation of a densely sintered body increases the efficiency of heat transfer and, as a result, intensifies the melting process. Consequently, by using non-metallurgical alumina a vitreous phase of larger volume obtains at the early stages of glass formation than with metallurgical alumina, disthene, and kaolin.

At 1100°C the products of heat treatment of the charge with all compositions are a vitrified body with the crystalline phase predominating, including the refractory components of the charge and the products of their interaction. According to XPA data, quartz predominates in the crystalline phase, magnesium and calcium aluminosilicates are also present.

On synthesizing samples using alumina the glass-making processes are completed at temperature 1280°C; homogeneity of glassy samples synthesized using disthene and kaolin is reached at 1300°C.

At the next stage of this work heat-treatment of the charge from 1250 to 1500°C was performed in a gas-fired batch-type crucible furnace without soaking as well as at 1300°C with soaking for 30 min and 1 h. On heat treatment of the charge in a gas-fired furnace the glass formation processes are completed at higher temperatures, which is due to a change in the heat treatment regime and heat transfer conditions. However, the predictable effects of the type of aluminum-containing raw material on the rate of glass-making processes are independent of the synthesis conditions. Glass formation processes in compositions containing alumina are completed at lower temperatures. At the heat treatment temperatures 1250, 1300, and 1350°C the largest volume of the residual crystalline phase is characteristic of the samples synthesized using kaolin.

TABLE 2. Volumetric Fraction of Phases in Glass Samples Synthesized at 1300°C and Different Soaking Times

Aluminum-containing raw material	Soaking time, h	Volumetric phase content, %		
		glassy	gaseous	crystalline
Metallurgical alumina	No soaking	83.3	11.3	5.4
Non-metallurgical alumina		93.2	3.0	3.8
Disthene		86.3	6.5	7.2
Kaolin		84.9	7.2	7.9
Metallurgical alumina	1	98.6	1.4	0.0
Non-metallurgical alumina		98.8	1.2	0.0
Disthene		98.5	1.3	0.2
Kaolin		96.5	2.7	0.8

The volume fractions of the crystalline, glassy and gaseous phases in samples heat treated at 1300°C with different soaking times are shown in Table 2. The metrics are determined on the basis of optical microscopy data and the density of the samples.

Soaking at 1300°C for 1 h leads to the completion of glass formation processes for samples synthesized using alumina. The largest volume of the crystalline and gas phases is characteristic of the samples synthesized with the use of kaolin. With an increase of the soaking time the volume fraction of crystalline and gaseous inclusions decreases from 15.1 to 3.5%. Faster glass formation and fining processes are achieved when using non-metallurgical alumina as compared with other types of aluminum-containing raw materials.

Samples of glasses synthesized using disthene and kaolin at 1500°C have an intense green color. If 0.1 wt.% iron oxides are added to the charge containing alumina with raw materials, then 0.25% and 0.31% are added when using disthene and kaolin, respectively. The heightened content of iron oxides in the glass melt reduces its diathermancy. The consequence of this is an increase in the volume fraction of the gaseous phase, equal to 0.91 – 0.92% for glass samples syn-

TABLE 3. Results of Thermal Analysis of the Charge

Process	Temperature of the endo peak, °C, when using aluminum-containing raw materials			
	metallurgical alumina	non-metallurgical alumina	disthene	kaolin
Decomposition of boric acid	138.6 167.0	132.7 163.5	128.8 163.4	128.1 164.4
Decomposition of $Al(OH)_3$	–	286.8	–	–
Decomposition of kaolinite	–	–	–	516.8
Polymorphic transformations of quartz	575.5	575.2	574.2	575.2
Decomposition of carbonates	821.5	813.1	802.8	808.3
Melting	964.5	956.7	944.0	1016.4

thesized using disthene and kaolin, which is significantly greater than in glass synthesized using alumina (0.36%).

A charge with the inclusion of various types of aluminum-containing raw materials was studied by means of differential scanning calorimetry in argon on a DSC 404 F3 Pegasus calorimeter from NETZSCH. As a result of studying the charge, DSC curves and the temperature dependences of the specific heat capacity were obtained in the temperature range 30 – 1400°C. The DSC results of the studied materials are presented in Table 3.

The investigated raw material compositions are characterized by the presence of endothermic effects in the temperature range 90 – 210°C, which are due to the stepwise decomposition of boric acid and the removal of physically bound water. In the composition containing non-metallurgical alumina an endothermic effect is present in the temperature range 230 – 330°C, due to the decomposition of impurity $Al(OH)_3$ with the formation of γ-Al_2O_3. In a composition with kaolin the endothermic effect with a maximum at 516°C is due to the decomposition of kaolinite. The endo effects in the temperature range 680 – 890°C are due to the decomposition of magnesium and calcium carbonates, respectively. Subsequent heating of the materials was accompanied by endothermic softening of the resulting amorphous material at temperatures 895 – 815°C and subsequent melting of crystalline substances at temperatures above 940°C.

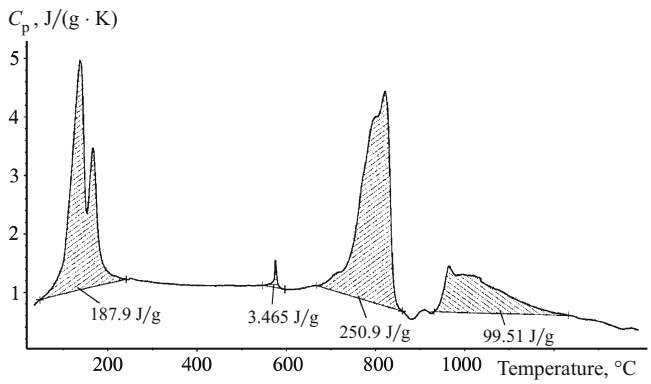

Fig. 1. Determined thermal effects on heat treatment of a composition containing metallurgical alumina.

TABLE 4. Specific Heat Capacity of the Test Samples

Alumina-containing raw material	Specific heat of the test samples, kJ/(kg · K), in the temperature range, °C		
	30 – 700	700 – 1000	1000 – 1350
Metallurgical alumina	1.12	1.03	0.96
Non-metallurgical alumina	1.08	0.99	0.90
Disthene	1.11	1.17	1.29
Kaolin	1.10	1.09	0.99

For a quantitative assessment of the efficacy of using various types of aluminum-containing raw materials, the heat consumption for glass formation processes was determined.

The authors of [2] estimated the heat consumption for melting boron-free and borosilicate glasses of type-E by a method that included a calculation of the material and heat balance of the glass-making process.

In [1] a model allowing the prediction of the thermodynamic characteristics of industrial multicomponent glasses and melts is proposed and the role of raw materials in the process of obtaining E-glass is considered.

In the present work a method is proposed for determining the heat consumption for the glass formation process, Q_{st}, including a calculation of heat consumption for heating the charge and molten glass, for chemical processes, and for heating gaseous decomposition products of the charge components.

The heat consumption on heating material to the melting temperature was determined from measurements of the specific heat of the studied materials (Table 4) according to the following formula:

$$Q_{ini} = (G_i^{fin} t_{fin} - G_i^{ini} t_{ini}),$$

where G_i is the mass of material entering the furnace, kg; G_i^{fin} and G_i^{ini} are the specific heat capacity of the material at the final and initial temperatures, kJ/(kg · K); and, t_{fin} and t_{ini} are the final and initial temperature of the computational period, °C.

Figures 1 – 4 show the temperature dependences of the specific heat capacity C_p at constant pressure, according to which the amount of absorbed energy during physicochemical processes in the studied raw materials is determined.

Table 5 shows the thermal effects determined for the processes occurring during the heat treatment of the studied materials in the temperature range 30 – 1400°C.

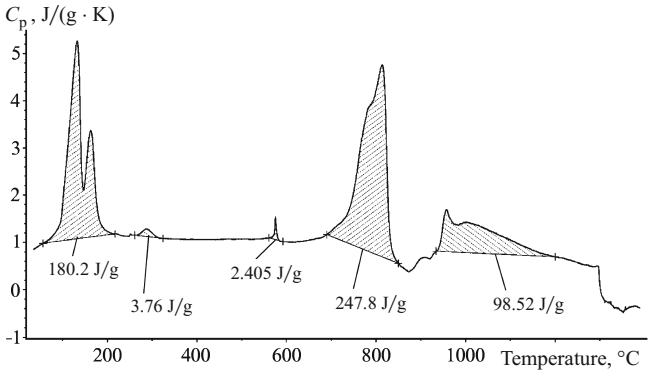

Fig. 2. Determined thermal effects on heat treatment of a composition containing non-metallurgical alumina.

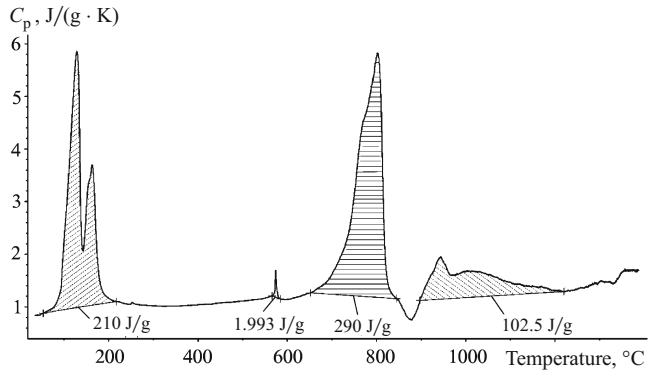

Fig. 3. Determined thermal effects on heat treatment of a composition containing non-metallurgical disthene.

The heat consumption for heating the decomposition gases $Q_{\text{h.d.g}}$, kJ/kg of glass melt, is determined from the formula,

$$Q_{\text{h.d.g}} = \sum V_{\text{gas}} C_{\text{gas}}\, t_{\text{gas}},$$

where V_{gas} is the volume of gas entering the furnace, m^3; C_{gas} is the heat capacity of gaseous decomposition products and water vapor at the temperature t_{gas} of decomposition products.

The amount of gaseous decomposition products and water vapor V_{gas} is determined according to the composition of the charge separately for all decomposition products (CO_2, SO_2, N_2O_5, etc.) according to the formula, m^3:

$$V_{\text{gas}} = \frac{M_{\text{c}} \times \text{LOI}}{100\rho_{\text{gas}}},$$

where LOI denotes losses on ignition of the component included in the composition of the charge, wt.%, and ρ_{gas} is the gas density, kg/m^3.

The computational results are presented in Table 6.

Table 7 shows the computational results for the heat consumption on glass formation processes during melting of

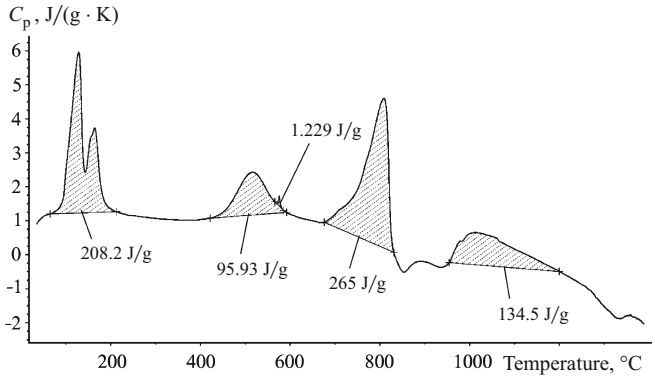

Fig. 4. Determined thermal effects on heat treatment of a composition containing kaolin.

type-E glass using various types of aluminum-containing raw materials. The lowest heat consumption obtains on using non-metallurgical alumina; correspondingly, the additional costs are determined in relation to the heat costs when using aluminum-containing raw materials of this type.

In a comparative assessment of the use of different types of aluminum-containing raw materials in the production of

TABLE 5. Determined thermal effects on heat treatment of test materials in the temperature range 30 – 1400°C

Process	Specific thermal effect of processes occurring in the test samples, kJ/kg (J/g), on using aluminum-containing raw materials			
	metallurgical alumina	non-metallurgical alumina	disthene	kaolin
Removal of physically bound water and decomposition of boric acid	–187.90	–180.20	–210.00	–208.20
Decomposition of $Al(OH)_3$	–	–3.76	–	–
Decomposition of kaolinite	–	–	–	–94.70
Polymorphic transformations of quartz	–3.46	–2.41	–1.99	–1.23
Decomposition of carbonates	–250.90	–247.80	–290.00	–265.00
Melting	–99.51	–98.52	–102.50	–134.50
Total	–541.77	–532.69	–604.49	–703.63

TABLE 6. Properties of Gaseous Decomposition Products and Their Amount

Gaseous product	Density, kg/m^3	Specific heat capacity, kJ/(m^3 · K)	Amount of gaseous decomposition products $V_{gas} \times 10^2$, m^3/kg of glass, on using aluminum-containing raw material			
			metallurgical alumina	non-metallurgical alumina	disthene	kaolin
CO_2	1.977	2.3355	8.96	8.96	8.92	8.94
SO_2	2.852	2.2777	0.23	0.23	0.24	0.16
H_2O	0.804	1.8327	10.95	11.00	10.77	16.96

TABLE 7. Heat Consumption on Glass Formation Processes

Heat consumption items	Heat consumption, kJ/kg of glass, on using aluminum-containing raw materials			
	metallurgical alumina	non-metallurgical alumina	disthene-sillimanite concentrate	kaolin
Heating of charge and molten glass	1395.99	1337.97	1545.78	1412.64
Chemical processes	541.77	532.69	604.49	703.63
Heating of decomposition gases	622.73	623.96	617.08	784.94
Total	2560.49	2494.62	2767.35	2901.21
Additional costs, %	2.64	0	10.93	16.30

type-E fiber, the best economic efficiency metrics within the framework of the study were obtained for non-metallurgical alumina White Alumina supplied by VAST-ECO Chemicals Company. In comparison with other studied samples of aluminum-containing raw materials, the use of non-metallurgical alumina affords savings of energy resources for glass formation processes from 2.64 to 16.30%.

The efficacy of non-metallurgical alumina is due to a number of factors. The high dispersion of this type of alumina and the presence of the reactive modification γ-Al_2O_3 along with Al_2O_3 in its phase composition accelerates the formation of aluminosilicates and melting of eutectic mixtures on heat treatment of the charge, while the formation of a densely sintered body makes heat transfer and therefore the glassmaking process more efficient.

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