Comprehensive comparative assessment of technological, physical, chemical and environmental properties of glass for the production of E-glass fiber with boron and without boron

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ABSTRACT

The research results of the boron-containing and boron free glasses of the E type for production of continuous glass fiber are presented. It was established that boron-containing glass has technological advantages due to more intensive glass melting processes, and its production process according to environmental indicators is comparable to boron-free glass production indicators.

INTRODUCTION

Manufacturers of continuous glass fiber produce two types of E-glass fiber that is boron-containing and boron-free ones obtained on the basis of $MgO–CaO–Al_2O–B_2O_3–SiO_2$ and $MgO–CaO–Al_2O_3–SiO_2$ systems respectively. The evolution of compositions of E-glass fiber is related to solving technological and environmental problems in production thereof and to reducing the cost of the raw material. Modification of the original E-glass by introducing boron oxide in an amount of up to 10 wt. %, as well as fluorine compounds was aimed at reduction of the melting temperatures and the upper crystallization limit temperature [1].

The most common alkali-free aluminum borosilicate E-glass have the following chemical composition, wt. %: SiO_2 52.0–56.0; Al_2O_3 12.0–16.0; B_2O_3 5.0–10.0; MgO 0–5.0; CaO 16.0–25.0; Na_2O+K_2O 0–2.0; TiO_2 0–1.5; Fe_2O_3 0–0.8; F^- 0–1.0 [1–4]. Boron-containing E-glass fiber combines high mechanical strength and dielectric properties with rheological properties ensuring stable process of fiber formation in a wide range of linear density. Boron-free compositions of E-glass comprise, wt. %: SiO_2 54.0–65.0; Al_2O_3 9.0–15.0; MgO 0–4.0; CaO 17.0–25.0; Na_2O+K_2O 0–2.0; F^- 0–0.5. Besides, TiO_2, Li_2O, ZnO, BaO and SrO are introduced into the glass compositions to regulate the technological properties. The best-known boron-free E-fiber is Advantex® of Owens Corning Corp. [2–4].

Development of boron-free glass compositions for insulating E type fiber is primarily aimed at solving environmental problems associated with volatilization of boron compounds. However, the elimination of B_2O_3 in the composition of glass increases melt viscosity, molding temperature and, consequently, energy consumption during its production. Analysis of the data on fiber glass composition and properties demonstrates that molding temperature for boron-containing glass amounts to 1140–1180°C, for boron-free glass it is at least 1260°C, and the crystallization temperature amounts to 1050–1065°C and 1180–1200°C respectively [2, 5]. The importance of boron oxide in regulation of technological properties is confirmed by the following data: introduction of 1.0 wt. % boron oxide into a boron-free glass composition for glass fiber results in decrease in the molding temperature by 32°C. Increase of the boron oxide content by 1.0 wt. % in borosilicate glass results in decrease of the fiber molding temperature by an average of 12 °C.

The current work is focused on comprehensive assessment of technological and physical-chemical properties of boron-containing and boron-free E-glass, and production ecology of continuous fibers based on them.

METHODS

Glasses synthesis

Borosilicate and boron-free glass was synthesized for comparative analysis of technological properties of glass for E-glass fibers. The composition of borosilicate glass comprises, wt. %: SiO_2 53.6–58.0; Al_2O_3 14.2; B_2O_3 3.1–9.0; MgO 1.4–2.7; CaO 19.55–22.35; Na_2O+K_2O 0.5; Fe_2O_3 0.15; F^- 0.3. Colemanite 75 micron produced by ETIMADEN IGM was used as boron-containing raw material. The chemical composition of colemanite includes, wt.%: B_2O_3 40.2; CaO 27.3; SiO_2 5.2; MgO 3.0; Al_2O_3 0.2; Fe_2O_3 0.04; R_2O 0.05; other 24.01.

Boron-free E-glass contain, wt. %: SiO_2 60.0–61.4; Al_2O_3 12.0–13.3; MgO 2.6–2.9; CaO 22.3–22.9; TiO_2 0–0.4; Fe_2O_3 0.3; Na_2O+K_2O 0.8. The compositions of boron-free glass are variations of the glass composition for Advantex® fiberglass from Owens Corning Corp.

Glasses were prepared by the melt-quenching technique. The synthesis was performed at the maximum temperature of 1500 °C in a gas furnace. Molten glasses were cast on the steel surface and then the obtained samples were annealed at 650 °C for 4 h in the muffle furnace in air to reduce stresses.

Measurements

The differential scanning calorimetric measurements have been performed by TGA/DSC-1/1600 HF and measuring unit DSC 404 F3 Pegasus. The heating range was up to 1400°C at a speed of 10 °C/min. Synthetic air was used as the reaction atmosphere.

The crystal structure was investigated by X-ray diffraction measurements using diffractometer D8 Advance with CuKα radiation source. The software DIFFRACPLUS from Bruker package was used to identify crystalline phases.

The viscosity of glasses in the range of 10^4–10^{10} Pa·s was determined by the method of compression of glass cylinder using an Orton PPV-1000 viscometer.

The glass transition and glass-softening points of the glasses were measured using DIL 402 PC quartz dilatometer in the temperature range 20–850 °C.

The assessment of the chemical resistance of the fibers was carried out according to the test results of the elementary fibers for tensile strength after their treatment in various aggressive media. Distilled water and alkaline solution with pH 12.9 (including NaOH and KOH) were used as aggressive media. Exposure of the fiber bundles in these media was carried out for 1, 7, 30 and 60 days. After chemical treatment, a tensile strength test of elementary fibers was carried out.

RESULTS AND DISCUSSION

For studying glass melting processes during test glass synthesis positional heat treatment of the charge was performed at temperature range of 700–1500°C. Visual assessment of the quality of batch for heat treatment of the boron-containing products has demonstrated that with an increase in B_2O_3 content from 3.1 to 9.0 wt. % the temperature of obtaining homogeneous melt free of crystalline inclusions decreases from 1400 °C to 1300 °C. Under the identical heat treatment conditions, the boron-free glass-forming process is completed at a temperature of 1450 °C. Comparison of thermal and X-ray phase analysis data has revealed the following sequence of phase transformations in the process of synthesis of the glass containing 9.0 wt.% of B_2O_3, introduced by colemanite, and boron-free glass Advantex®.

Decomposition of the colemanite basic substance $Ca_2B_6O_{11} \cdot 5H_2O$ in the batch of type E borosilicate glass in the temperature range of 300–450 °C occurs in accordance with the following scheme: $Ca_2B_6O_{11} \cdot 5H_2O \rightarrow 2CaB_2O_4 + B_2O_3 + 5H_2O$. Formation of calcium borates, calcium and magnesium silicates begins with chalk and dolomite decarbonization processes.

Occurrence of calcium borate ($Ca_3B_2O_6$), calcium silicate ($CaSiO_3$) and anorthite ($Ca[Si_2Al_2O_8]$) is recorded at temperatures of 900°C. Formation of eutectic melts between calcium borate and other compounds facilitates active melting of the batch at temperatures of above 1000°C, dissolution of heat-resistant components of the system up to formation of homogeneous melt at the temperature of 1300°C. Boron oxide in course of silicate and glass formation processes is mainly in chemically bonded state: colemanite → calcium borate → calcium borosilicate. This predetermines reduction of high-temperature volatility of boron compounds. In a series of parallel experiments by means of gravimetric method, it has been found that volatilization is on average 32 % less when using colemanite than with the use of boric acid. Pyroxene ($CaMgSi_2O_6$) is found in the batch of type E boron-free glass at heat treatment temperatures of above 1100°C. Eutectic melts and melting of the batch occur at temperatures of above 1100°C. Glass melt becomes homogeneous in a temperature range of 1400–1450°C.

An assessment of the heat input for glass formation process in production of boron-free and borosilicate E-glasses has been performed in accordance with the technique used in the thermotechnical calculations. The technique includes calculation of material and thermal balance of the glass melting process [7]. It was established that heat consumption for glass melting processes, all other conditions being equal, for boron-free glass is 3385.6 kJ/kg of molten glass, which is 14.3 % more than for borosilicate E-glass, heat consumption for which being 2901.45 kJ/kg of molten glass.

At studying the glass by viscometry method it was established that boron oxide content decrease in borosilicate glass composition leads to expectable viscosity increase within all the temperature range, which is particularly significant in temperature range of melting and fiber formation. The viscosity gradient increases with temperature increase upon transition to thinly fluid state – above the Littleton temperature, i.e., at a viscosity of more than $10^{6.6}$ Pa·s.

If we compare the characteristic temperatures of glasses with of 9.0 wt.% B_2O_3 content and the boron-free composition, then these temperatures are significantly higher for the boron-free composition: glass-transition temperature (T_g) increases from 692 °C up to 750 °C, Littleton temperature – from 852 °C to 900 °C, which is a result of increased low-temperature viscosity. The high-temperature viscosity increases most significantly for boron-free composition in comparison with the boron-containing composition: the temperature corresponding to the working viscosity of 10^2 Pa·s increases from 1180 °C to 1260°C, the practical melting point corresponding to the viscosity of 10 Pa·s – from 1346°C to 1440°C.

Temperature range of boron-free glass crystallization is shifted towards higher temperatures: the upper crystallization temperature for Advantex® boron-free glass composition is 1227°C whereas for borosilicate glass with 9 % content of boron oxide it is 1150°C. Accordingly, temperature for boron-free fiber formation must be 60–80°C higher than that of boron-containing fiber.

In accordance with the experimental data, the temperature of formation of fiber from boron-free glass composition is 70–90 °C higher than from borosilicate glass containing 6.0–9.0 wt. % of boron oxide. Practical melting point is significantly higher as well. Consequently, reduction of the boron oxide content in glass composition or its complete elimination requires additional measures to intensify the glass melting process in order to ensure the desired performance of the glass-melting furnace. Increase in fiber production temperature causes increase in energy consumption at this technological stage of production, and intensifies the processes of sublimation and dissolution of platinum-iridium alloy – feeder material - in the glass melt.

For comparative assessment of E-glass according to specified parameters, roving produced by different manufacturers was tested, obtained from Advantex® boron-free glass and boron-containing E-glass. The breaking load at testing boron-containing glass roving is 1270 H, of Advantex® boron-free roving – 1260 H. As evaluation criterion of chemical resistance of the

fibers, tensile strength after their treatment in different media was adopted, due to its importance for composite materials. Distilled water and alkaline solution with pH 12.9 were used as aggressive media. Adjusted for coefficient of variation, the strength of boron-containing and boron-free fibers prior to testing is on the same level and equals 2400–2560 MPa. The results of determination of the fibers strength after exposure to water are presented in Fig. 1, in which the horizontal dashed lines demonstrate the strength values range of the control samples not subjected to processing.

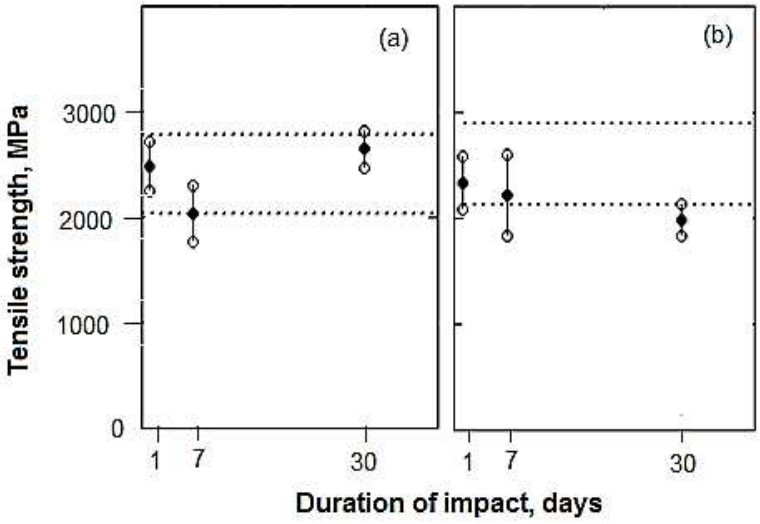

Fig. 1: The strength of boron containing (a) and boron-free (b) fibers after exposure to water

Exposure to water for 7 days results in almost the same level of strength reduction for boron-containing and boron-free fibers. When exposed to alkaline solution, the strength reduction occurs both for boron-free and boron-containing fibers. The strength reduction degree amounts to 1.7 and 2.7 times for fiber and boron-containing fiber respectively when exposed for 30 days (Fig.2). The strength reduction is due to the increase in the number of defects on the fiber surface. Violation of the initial structure and chemical composition of the fibers can be considered as the probable causes of defects after chemical exposure.

The major sources and types of emissions to the environment in boron-containing and boron-free fibers production have been identified when assessing the ecology of the production. The main pollutants in the glass fiber production are the following: dust and fibers, oxides of nitrogen, carbon and sulfur, oxides of heavy metals, with 80–90% of the gross emissions accounted for glass melting furnaces [8].

To compare the impact on the environment in production of glass fiber, the amount of emissions in the following production options has been calculated: production of E-type boron-containing glass with 9 wt.% B_2O_3 content introduced with colemanite in a recuperative glass melting furnace and production of boron-free glass in recuperative glass melting furnace.

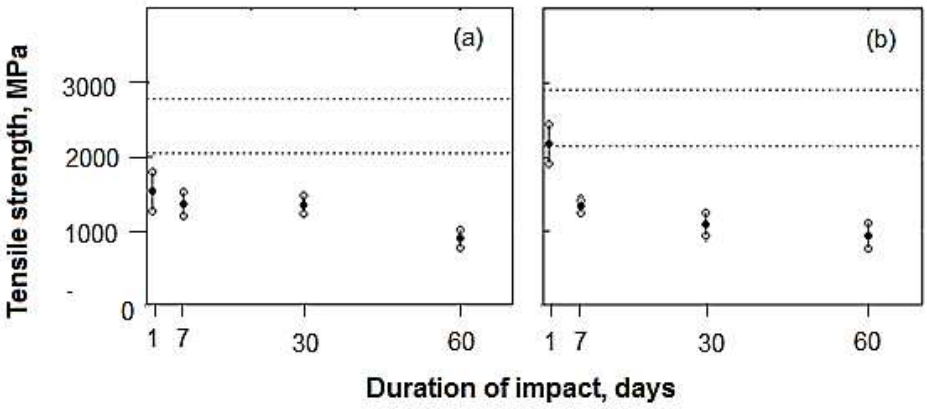

Fig. 2: The strength of boron containing (a) and boron-free (b) fibers after exposure to alkaline solution

The emissions composition includes inorganic dust, nitrogen oxides, carbon monoxide, and boron and fluorine compounds in the case of boron-containing glass. The main causes of the nitrogen oxides emissions are formation of thermal NO_x at high temperatures in the furnace and oxidation of the nitrogen contained in the fuel. Sulfur dioxide (SO_2) in the exhaust gases of glass melting furnaces is determined by the content of sulfur in the fuel and raw materials. Emissions of boron oxide and fluorine compounds are related to volatility of the batch components such as boric acid and fluorine in SiF_4 compounds. *Generally, accepted techniques have been used to calculate the amount of the emissions.* Since the heat input for the boron-free glass formation process is 14.3 wt. % higher than for the boron-containing one, the amount of natural gas required for production of 1 ton of the glass fiber was increased proportionally during the calculations.

Calculation of the coefficient (criterion) C, taking into account the volume and danger of emissions was performed to assess the environmental impact of the industries:

$$C = \sum_{i=1}^{n} \left(\frac{M_i}{TLV_{ce}} \right)^{\alpha_i},$$

where n is the amount of pollutants entering the air from stationary sources of emissions; M_i is the mass of the i-th pollutant, kg/t of glass; TLV_{ce} (Threshold Level Value continuous exposure) is the average daily maximum permissible concentration of the i-th pollutant in the air, mg/m^3; α_i is a nondimensional constant that allows to correlate the degree of impact of the i-th pollutant with the impact of the third hazard class pollutant.

It has been found that glass melting in recuperative furnace makes the greatest impact on the environment. This criterion amounts to 370 for boron-containing E glass, which is associated with a decrease in gas consumption and, accordingly, a decrease in nitrogen oxides emissions at the glass melting stage. Emissions of boron oxide in the production of E-type glass in glass-melting furnaces amounts to 0.4 kg/t, the total contribution of boron compounds to the design C criterion, including colemanite dust, amounts to 3.4% when melting glass in a recuperative furnace. The use of colemanite instead of boric acid as a boron-containing raw material reduces the C criterion performance by 10 units due to decrease in boron compounds volatilization.

CONCLUSIONS

The research results of the boron-containing and boron free glasses of the E type for production of continuous glass fiber are presented. Technological, technical and ecological benefits of the boron-containing glass are shown. In the study of vitrification processes, it was established that

with identical temperature-temporal modes of synthesis, glass melting processes are intensified with an increase of boron oxide content in glass compositions. The formation of eutectic melts between borates, silicates and aluminosilicates promotes the batch melting at 1000–1100 °C and the transformation of a heterogeneous material mixture into thehomogeneous melt at 1300 °C. In the synthesis of boron-free glass, vitrification processes are completed at 1400-1500 °C. High-temperature viscosity and the top crystallization temperature is higher in comparison with boron-containing glass composition that requires the temperature increase of forming continuous fiber from boron-free glass by 60–80 °C. As the whole, that causes the higher energy expenses for its production. When testing fiberglass rovings produced from boron free and boron-containing E-glasses of various manufacturers, it was established that their strength is at the same level, including the rovings after exposure to water and alkaline solution. Ecological aspects of production of boron-containing and boron free glasses of the E type were discussed.

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