Influence of boron-containing components on processing of basalt melts and glasses

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ABSTRACT

The research results of the technological properties of basalt melts and glasses produced based on basalt – colemanite compositions are presented. It was established the possibility of reducing the temperature of continuous glass fibers production, due to a lower viscosity, liquidus temperature and crystallization ability of the melt. The prospects of using colemanite produced by ETIMADEN IGM in the production of basalt fiber were shown.

INTRODUCTION

The use of basalts as a raw material for manufacturing of continuous fiber is of great prospect. Basalt fiber is a material combining high mechanical strength, corrosion resistance to aggressive media, high heat resistance and a relatively low cost. Basalt fibers breaking strength indicator is 3000–4840 MPa, and modulus of elasticity is 79.3–93.1 GPa. Basalt fibers not only possess good mechanical properties, but can be used in a wide temperature range from minus 260 to 700 °C as well. Basalt fiber can be attributed to high strength fibers on mechanical properties and compete with the carbon fiber in terms of the indicators of stability [1–3].

The basalt fibers have a wide range of applications as heat and sound insulating materials, as well as a composites reinforcing material. Basalt continuous fiber based composites are characterized by high impact resistance and resistance to alternating loads, as well as by corrosion and thermal resistance. It is currently one of the most preferred materials for applications in aerospace and automotive industries, construction, chemical and petrochemical industries [1].

The difference in continuous basalt fibers properties is due to the difference in their compositions, including wt. %: SiO_2 45.9–58.7; Al_2O_3 8.2–18.6; $FeO+Fe_2O_3$ 2.8–15.0; CaO 5.0–16.0; MgO 1.3–14.2; Na_2O+K_2O 3.0–7.5; TiO_2 0.9–3.2; P_2O_5 0.1–0.8; MnO 0.1–0.6 [2]. A number of criteria for appropriateness of earth materials used for continuous basalt fiber manufacturing are available. Chemical and mineral composition of basalts, i.e. viscosity and crystallizability, which determine the technological properties of basalt melts, is of vital importance [3–4]. Temperature and time of exposure of the melt affect the structural homogeneity of basalt glass. The presence in the melt of crystalline inclusions with incomplete dissolution of such minerals as quartz, pyroxenes, etc. leads to decrease in the strength of the fiber [5].

The potential benefits of continuous basalt fiber as material with high level of physical and chemical properties necessitates improvement of technology of its production. Instability of chemical composition, rheological properties and enhanced ability of crystallization of basaltic melts predetermine high temperatures of fiber formation and instability of molding process.

The current work is focused on improving the technological properties of basalt glasses and melts by modifying their composition. Ground colemanite produced by ETIMADEN IGM was used as modifying component.

METHODS

The chemical composition of colemanite includes, wt. %: B_2O_3 39.90; CaO 26.92; SiO_2 5.28; MgO 2.79; SrO 1.32; Al_2O_3 0.15; Fe_2O_3 0.05; R_2O 0.11; SO_3 0.20; other 23.28. To obtain basalt fibers used basalt with composition, wt. %: SiO_2 54.03; Al_2O_3 18.21; FeO+Fe_2O_3 9.96; CaO 7.94; MgO 3.63; Na_2O 2.51; K_2O 2.03; TiO_2 1.12; P_2O5 0.17; MnO 0.16. The basalt–colemanite compositions include 5–20 weight fractions of colemanite, with which 2–8 wt.% B_2O_3 is introduced.

The melting of basalts and basalt-based compositions was performed the traditional way at the maximum temperature of 1480 °C for 2 h in a gas furnace. Molten basalts and basalt-based compositions were cast on a steel surface, and then the obtain glass samples were ground to particles of 5–20 mm in size, depending on the subsequent method of investigation, and besides were used to form fiber based on them.

The melting temperature of basalts and compositions based on them was determined during heat treatment in a gradient furnace, in which zones with a stable temperature gradient are created in the range of 800–1400 °C for 1 h.

The crystallization ability of basalt glasses was determined from the results of gradient heat treatment and thermal analysis data. Gradient crystallization was carried out in a gradient furnace in the temperature range of 600–1300 ºC.

The differential scanning calorimetric measurements (DSC) 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.

A RSV-1600 viscometer (Orton) was used to determine the high-temperature viscosity of basaltic melts via the resistance of a rotating platinum rod to the melt in a 2 K/min cooling regime.

The chemical resistance of basalt fibers was determined by the weight loss of the sample when exposed to the following reagents: distilled water or 2 N NaOH solution. The fibers were treated by boiling in a water bath for 3 h.

The strength of the single fibers was determined using the MTS Criterion 43.503 electromechanical tensile testing machine. It was tested at least 75 single fibers each composition.

RESULTS AND DISCUSSION

Basalt mineral composition includes plagioclases, which are anortite-based and albite-based solid solutions, pyroxene which is diopside-based solid solution, and magnetite. Encrusting matters of quartz and olivine ($(Mg, Fe)_2[SiO_4]$) are found as inclusions in separate samples. Basalt complete fusion melting point of 1400 ºC is predetermined by the availability of high-melting minerals. A significant decrease in the temperature to achieve a homogeneous melt has been evaluated on the basis of the research findings for the temperature range of basalt – colemanite compositions melting. Complete fusion melting point for compositions with 4.0 wt.% of B_2O_3 content does not exceed 1330 ºC; homogeneity of melts of the compositions with 6.0 and 8.0 wt.% of B_2O_3 content is achieved by heat treatment in the temperature range of 1300–1350 ºC.

According to DSC data, colemanite is melted in the temperature range of 950–1075 ºC. Formation of low-viscosity liquid phase during melting of colemanite heat treatment products, represented by boron anhydride and amorphous substance, stimulates the dissolution of crystals of the basalt mineral matter. Reducing the surface tension of the melt when added B_2O_3 improves the wettability of grains with melt that also accelerates their dissolution.

Basalt glasses crystallizability has been evaluated by means of a complex method based on the results of gradient crystallization and differential scanning calorimetry data. Surface and bulk crystallization has been revealed based on the result of heat treatment of the glass samples. Phase composition of the bulk crystallization products is represented by anorthite ($CaAl_2Si_2O_8$) and albite ($NaAlSi_3O_8$). The upper crystallization temperature of the basalt-based glass amounts to 1285 ºC. It is dropped to 1160 °C by the increase of B_2O_3 content in the basalt glass composition. The upper crystallization temperature is an important technological characteristic, since the temperature range of fiber formation is limited by this parameter.

A number of exothermic effects associated with basalt glass crystallization have been recorded by means of the thermal analysis. According to the thermal analysis results, the glass transition temperature corresponding to transition of glass from solid to plastic stage at the viscosity of $10^{12.3}$ Pa·s as well as the glass-softening point have been evaluated. In addition, melting points of the crystalline materials segregated during heat treatment have been evaluated (Table 1).

Table 1. Thermal characteristics of glasses according to DSC.

Content B_2O_3	Glass transition	Glass-softening point	Crystallization	Melting of crystalline phases
(%)	(°C)	(°C)	(°C)	(°C)
0	654.9	686.1	856.0–1077.0	1144.2–1252.6
2	635.0	673.1	844.4–967.7	1096.8–1233.1
3	627.9	665.0	841.7–944.9	1109.2–1224.6
4	625.3	664.1	839.2–907.3	1096.4–1211.0
6	623.8	662.4	832.0–912.2	1078.7–1176.7
8	622.7	660.2	817.3–905.0	1073.0–1155.5

The crystallization process is the most active in the temperature range of 800–1000°C. With an increase of B_2O_3 content in the basalt glass composition, the crystallization temperature range is narrowed, and the exo-effects maxima intensity on the DSC curves is decreased. Consequently, modification of basalt glass results in decrease in liquidus temperature and crystal growth rate, i.e. a decrease in the tendency for crystallization. A decrease in liquids temperature, i.e. the temperature above which the spontaneous crystallization does not occur, allows the fiber formation temperature (operating temperature) to be decreased. From the technological point of view, the interval between the operating temperature and the melt liquidus temperature should be maintained within 50–100 °C [3].

Melts viscosity indicators are crucial in assessing their appropriateness for continuous fibers forming, as well as for determination of the optimal mode of forming. For this reason, rheological properties of melts are paid great attention when earth materials are evaluated [3, 4, 6]. Research results on basalt melts of modified compositions by means of viscosity measurements method is presented in Fig. 1.

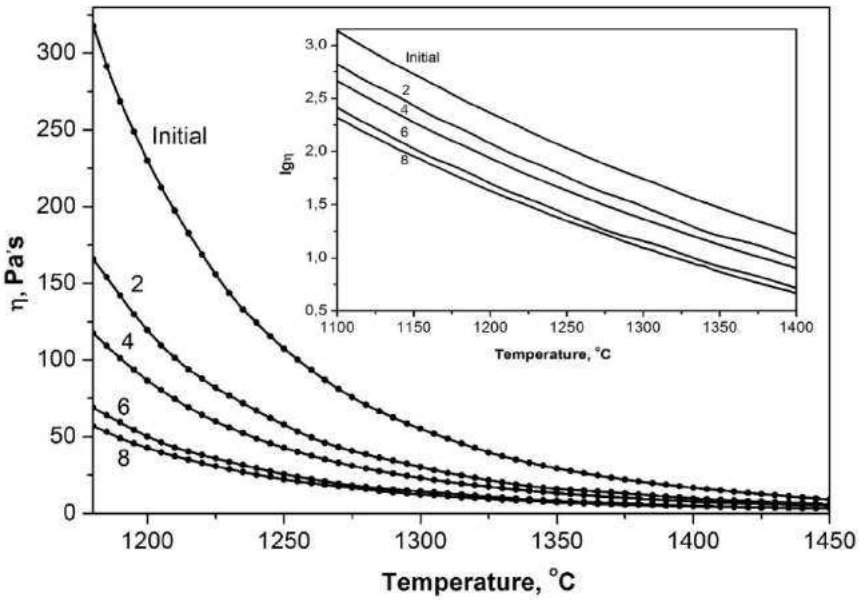

Fig. 1: Temperature dependence of melt viscosity (2–8 – content B_2O_3, wt. %)

While examining the basaltic melts it was established that combined impact of colemanite components causes substantial high-temperature viscosity reduction as its content in the composition increases. Melt viscosity indices decrease most significantly at content of B_2O_3 2–4 wt. %. Increase in B_2O_3 content from 4 to 8 wt. % causes a less pronounced decrease in the activation energy of a viscous flow. With an increase in B_2O_3 content, the viscosity gradient is decreased as well. Decrease in the boron-containing melts viscosity indicators in combination with reduced crystallizability allows reducing the temperature as well as extending the fiber formation temperature range.

Basalt fibers forming temperature corresponds to a viscosity lgη = 1.5 Pa·s [7]. For the melt of the initial basalt, this indicator is achieved at 1340 °C. With an increase of modifiers content in the melt composition, the forming temperature decreases, in particular when the content of B_2O_3 is 4 wt. % forming temperature is 1270 ° C; 8 wt. % –1220 °C. The interval between the forming temperature and the liquidus temperature (upper crystallization temperature) of the modified melts is 50–80 °C, which corresponds to the conditions for ensuring a stable fiber forming process.

In order to assess the impact of B_2O_3 on the ability of basaltic melts to fiberize, experimental work in obtaining modified basalt fibers was conducted. In the results of drawing fibres from the glass melts based on basalt and basalt–colemanite compositions it was established that as boron content increases in the basalt glass composition, the formation process becomes more stable, the fiber breakage rate reduces and its quality improves. The processes of forming continuous fibers with 4 and 6 wt. % boron oxide content are the most stable one.

The impact of boron oxide on performance characteristics of boron-containing basalt fibers obtained at the laboratory unit was established according to results of research of their chemical resistance and strength.

Chemical resistance indicators of the glass fibers are affected by a number of factors, such as fibers composition; reagent composition, concentration and volume; temperature and duration of chemical treatment; fibers surface condition. In this regard, chemical stability indicators of basalt fibers can vary in a reasonably large range of values. The research results on basalt fibers chemical resistance obtained in a laboratory facility from melts of the earth materials from various deposits, with acid resistance being 50.4–89.7 %, alkali resistance – 76.3–91.4%, water

resistance – 99.3–99.8 %, are presented in the paper [8]. Modified basalt fibers have high water resistance levels – 99.4–99.6 %.

In case of aqueous corrosion, modifying cations, especially reactive ions of alkali metals are affected. In this case, an ionic exchange involving alkali metal ions and proton containing fluid components, i.e. hydrogen ions (H^+) or hydroxonium ions H_3O^+, (leaching process) occurs. «Nonbridging» oxygen ions exhibit high reactional availability as well [9].

Since the experimental basalt glasses are classified as low-alkaline ones (Na_2O content does not exceed 2.5%), the leaching process is not reactive, which determines the low mass loss when treated with distilled water. In addition, formation of insoluble film from $SiO_2 \cdot nH_2O$ on the glass surface prevents the cations diffusion and, as a result, the leaching process is decelerated.

Alkali resistance is 99.1–92.8 %, i.e., boron-containing and boron-free fibers have the same resistance level. An increase in CaO content in the glasses synthesized on basalt–colemanite compositions basis positively effects the alkali resistance indicators. When basalt glass is exposed to NaOH, the reaction product is sodium silicate Na_2SiO_3, which is hydrolyzed in aqueous solutions. Formation of insoluble hydrosol is possible in hot water. Formation of sodium metaborate $NaBO_2$ may result from glass interaction with NaOH in the event of B_2O_3 availability in the glass composition.

As can be seen from the above, it has been established that modification of basalt glasses by boron-containing components slightly affects water and alkali resistance indicators of the basalt fibers.

The method of estimation ultimate tensile stress of single fibers was used when testing the tenacity of the boron-containing basalt fibers. According to the estimated values, histograms of distribution the fibers strength under tension were plotted and the distribution law was selected. Left-sided symmetry of the graph was deduced, which is characteristic of the lognormal normal distribution of a random variable. The law is acceptable for the case of several influencing factors. In the given case, they are technological and structural factors, as well as a scale effect. If the first two factors are difficult to be described upon the fact of the samples manufacturing, the scale effect can be analyzed by plotting the dependence of the fiber strength on its diameter. When using two-base logarithmical coordinates, the linear dependence was accepted satisfactory to describe the scale effect for all batches. According to the test results, it has been established that the fibers strength is increased with an increase in the boron oxide content (Fig. 2). Strength testing of boron-containing basalt fibers proved influence of technological and structural factors, scale effect. It was established that with increase of the boron oxide content the fiber strength increases. Based on the dependencies received it can be concluded that at obtaining boron-containing basalt fibers with diameter 10 μm, fiber strength values more than 2100 MPa can be achieved for all compositions, which is at the level of known similar materials.

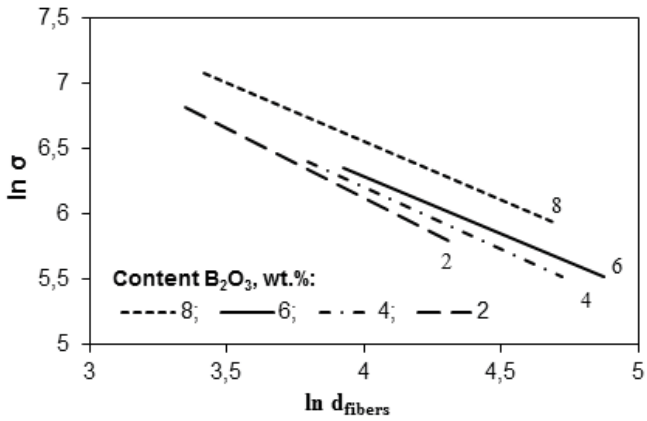

Fig. 2: The dependence of the tensile strength of the fiber on the fiber diameter and its composition

The increase in the boron-containing fibers strength alongside with an increase in boron oxide content is obviously due to the influence of the technological factor. The positive effect of the boron oxide on the quality of the fiber was determined during formation of fibers at a laboratory facility.

CONCLUSIONS

The performed tests of basalt–colemanite feed compositions and the glass based on them revealed following advantages of using colemanite in continuous basalt fiber production. Reduction of the melting temperatures of basalt–colemanite compositions, viscosity of melts and crystallization ability of glass with increase of boron oxide content makes it possible to reduce energy consumption. The optimum combination of technological properties of melts and glass, strength values, water an alkali resistance of the fibers is achieved by using basalt–colemanite compositions that contain 10–15 weight fractions of colemanite. The required level of properties is ensured by combined introduction of calcium and boron oxides into basalt glass composition.

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