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OPTIMIZATION OF THE BASALT GLASS COMPOSITION FOR THE CONTINUOUS FIBER PRODUCTION

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The paper studies the influence that Al_2O_3, B_2O_3, SiO_2 and CaO containing modifying components introduced in different combinations have on the technological and mechanical properties of basalt glass concerning their use in the production of continuous fibre. It is shown that introduction of boron-containing components into compositions with basalt accelerates achievement of structural homogeneity of the melt and reduces crystallization capacity of the glass. The viscosity and the upper crystallization temperature numbers that determine the technological parameters of fibre formation are determined. The elastic and strength properties of basalt glass were studied under static and cyclic loads. It is established that introduction of modifying aluminium-containing components ensures a 15–30% increase in the strength parameters. The optimal combination of technological and mechanical properties of basalt glass is achieved due to the use of compound modifiers with aluminium- and boron-containing components.

Keywords: basalt glass, continuous fiber, viscosity, crystallization, strength, alkali resistance

ОПТИМИЗАЦИЯ СОСТАВОВ БАЗАЛЬТОВЫХ СТЕКОЛ ДЛЯ ПРОИЗВОДСТВА НЕПРЕРЫВНОГО ВОЛОКНА

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В данной работе исследовано влияние модифицирующих компонентов, включающих Al_2O_3, B_2O_3, SiO_2 и CaO, вводимых в различных сочетаниях, на технологические и механические свойства базальтовых стекол применительно к использованию в производстве непрерывного волокна. Показано, что введение борсодержащих компонентов в состав композиций с базальтом ускоряет достижение структурной однородности расплава и снижает кристаллизационную способность стекол. Определены показатели вязкости и верхней температуры кристаллизации, определяющие технологические параметры формования волокна. Проведено исследование упруго-прочностных свойств базальтовых стекол при статических и циклических нагрузках. Установлено, что введение модифицирующих алюмосодержащих компонентов обеспечивает повышение показателей прочности на 15–30%. Оптимальное сочетание технологических и механических свойств базальтовых стекол достигается при использовании комплексных модификаторов, включающих алюмо- и борсодержащие компоненты.

Ключевые слова: цинксодержащий концентрат, прокалка, степень извлечения, сульфат цинка, серная кислота

UZLUKSIZ TOLA ISHLAB CHIQARISH UCHUN BAZALT SHISA TARKIBINI OPTIMALLASHTIRISH

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Ushbu ishda turli miqdorda kiritilgan Al2O3, B2O3, SiO2 va CaO saqlagan modifikatsiyalovchi komponentlarning uzluksiz tola ishlab chiqarishda qo'llaniladigan bazalt shishasining texnologik va mexanik xususiyatlariga ta'sirini o'rganilgan. Bor tarkibli komponentlar kiritilgan bazalt kompozitsiyalarda eritmaning strukturaviy bir xilligiga erishishni tezlashishi va shishalarning kristallanish qobiliyatini pasayishi keltirilgan. Tola olish texnologik parametrlarini belgilovchi yopishqoqlik va yuqori kristallanish harorati ko'rsatkichlari aniqlanadi. Statik va tsiklik yuklar ostida bazalt oynalarining elastik mustahkamlik xususiyatlari o'rganildi. Alyuminiy saqlovchi modifikatorlarni tarkibga kiritilishi mustahkamlik ko'rsatkichlarining 15-30% ga oshishini ta'minlashi aniqlandi. Bazalt shishalarining texnologik va mexanik xususiyatlarining optimal kombinatsiyasiga alyuminiy va bor saqlovchi komponentlarni birgalikda kiritish orqali erishiladi.

Kalit so'zlar: rux bazalt shishasi, uzluksiz tola, qattiqlik, kristallanish, mustaxkamlik, ishqorbardoshlik

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Introduction

Rocks of volcanic origin, such as basalts, basaltic andesites, etc., are widely used in the production of thermal insulation materials based on mineral wool. At present, the most promising material obtained from such rocks is continuous fibre. Wide prospects for application of continuous basalt fibre are attributable to the abundance of the raw materials in the nature, the environmental friendliness of the production and high level of strength, thermal resistance and chemical resistance of the materials based on it. In particular, basalt continuous fiber is an effective reinforcement material in the production of composites that are characterized by high level of strength and resistance to alternating loads. Basalt fibers breaking strength indicator is 3000–4840 MPa; modulus of elasticity is 79.3–93.1 GPa. Basalt fibers can be used in a wide temperature range from minus 260 to 700 °C as well and can be attributed to high strength fibers on mechanical properties [1–4].

However, there are a number of technological problems in the production of continuous fibre due to the instability of the chemical and mineral composition of basalt, the high absorption ability of iron -containing melt and the enhanced crystallization ability [5, 6].

Basalt continuous fiber produced directly from natural basalt rarely has good technological characteristics. Consequently, there are ongoing activities aimed at modifying the composition of basalts by way of introduction of additional components [7–10].

Optimization of basaltic glass composition is a topical direction of the technological innovations in the field of continuous basalt fiber production.

Glass composition plays an important role in determining the strength of high performance types of fibre. Owing to the increase of content of SiO_2 and Al_2O_3 in basalt fibre, due to the introduction of ZrO_2, La_2O_3, MgO and ZnO increase in strength, thermostability and chemical stability of basalt fibre was achieved. However, the melting points of raw material mixtures and the fibre formation temperatures thereby significantly increased [5, 9, 11–14].

The technological properties of basalt melts are optimized through the use of rock mixtures, as well as by adding pyrophyllite, diopside and calcium carbonate [8, 9].

The use of colemanite in order to modify the composition of basalt glass for continuous fibre ensures improvement of the technological properties of the melts, thanks to which reduction in energy consumption for production of continuous basalt fibre is achieved [15, 16].

Research methods

Basaltic andesites from Podgornyanskoye deposit were used for basaltic glass production. According to the results of analysis of chemical composition of basalts conducted by atomic emission spectroscopy method with a laser analyzer LEA-S500, average composition of basalts includes, wt.%: 53,0 SiO_2; 17,22 Al_2O_3; 12,33 Fe_2O_3; 8,28 CaO; 4,07 MgO ; 4,02 R_2O; 1,08 TiO_2.

Basalt mineral composition includes plagioclases, which are anortite-based ($CaA_{l2}Si_2O_8$) and albite-based ($NaAlSi_3O8$) solid solutions, pyroxene which is diopside-based ($CaMgSi_2O_6$) solid solution, and magnetite (Fe_3O_4).

Basalt glasses were synthesized based on compositions basalt – modifier. The following materials were introduced as modifying materials: disthene-sillimanite concentrate (disthene), alumina and colemanite.

The content of oxides in compositions varies within the following limits, wt.%: 47,33–53,00 SiO_2; 15,29–23,61 Al_2O_3 ; 11,43–12,53 Fe_2O_3 ; 7,66–10,63 CaO; 3,78–4,09 MgO; 3,67–4,16 R_2O; 0–4,39B_2O_3.

The melting of basalts and basalt-based compositions was performed the traditional way at the maximum temperature of 1500±10 °C in a gas furnace. The temperature rise in the furnace was carried out at a rate of 250 °C/h, gaseous atmosphere is oxidative; air excess factor is 1.08–1.13.

In order to identify the peculiarities of the process of melting basalt-modifier raw material compositions positional heat treatment was performed in gas furnace at 1250 and 1350 ^oC.

Chemical composition of raw basalt-based compositions is listed in Table 1.

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 SP30/13 in the temperature range of 800–1300 ^oC.

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 «Match!» was used to identify crystalline phases.

Table 1

Chemical composition of basalt-based compositions

Composition no.	Content of components, wt. %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	B_2O_3	MgO	Na_2O	K_2O	TiO_2
1	53,0	17,22	12,33	8,28	–	4,07	2,52	1,50	1,08
2	50,98	20,35	11,83	7,98	–	3,94	2,51	1,44	0,96
3	48,89	23,61	11,35	7,66	–	3,78	2,41	1,38	0,92
4	49,09	14,66	12,01	10,63	4,39	4,26	2,37	1,46	1,11
5	50,29	15,08	12,35	9,92	3,01	4,28	2,43	1,49	1,14
6	50,92	15,29	12,53	9,54	2,29	4,28	2,47	1,52	1,16
7	48,61	19,81	11,96	9,11	2,19	4,09	2,36	1,45	1,11
8	47,33	21,24	11,65	8,87	2,13	3,98	2,30	1,42	1,08
9	50,00	18,74	11,58	8,80	2,11	3,96	2,27	1,40	1,10
10	49,44	18,50	11,43	9,15	2,78	3,95	2,24	1,38	1,08

Table 2

Indicators of glass properties

Composition no.	Upper crystallization temperature, °C	Viscosity Modulus	η 1300, Pa·s	η 1400, Pa·s	Strength, MPa	Alkali resistance, %
1	1275	2,64	35,73	11,42	124	2,9
2	1315	2,81	46,34	14,62	140	3,1
3	1290	2,98	58,77	18,62	164	3,2
4	1235	2,05	12,05	4,09	127	2,4
5	1248	2,11	13,93	4,68	126	2,5
6	1255	2,20	16,51	5,49	123	2,7
7	1286	2,57	32,89	10,48	148	2,8
8	1320	2,74	37,47	12,22	151	2,9
9	1282	2,49	27,89	9,02	137	2,8
10	1285	2,40	23,76	7,75	148	3,0

The bending strength of glass under static and cyclic loads was determined using the electromechanical tensile testing machine Galdabini Quasar 100. During cyclic tests, after reaching the maximum specified load, it was reduced to 50 N. Then the loading-unloading cycle was repeated until the complete destruction of the material and the number of cycles was determined.

The chemical resistance of basalt glass was determined by the weight loss of the sample when exposed to the 2 N NaOH solution at 98 ºC.

Results and Discussion

The product of heat treatment of basalt at a temperature of 1250 °C is a vitrified mass containing crystalline inclusions ranging in size from 10 to 300 microns. The introduction of alumina and disthene into the composition causes an increase in the volume fraction of the crystalline phase. According to X-ray diffraction measurements, the crystalline phase is represented by relic plagioclase (labradorite). The increased crystallization ability of the glass associated with high content of iron oxides, leads to release of magnetite Fe_3O_4. Introduction of boron-containing components into the composition causes the melt to occur at lower temperatures. B_2O_3 significantly reduces the viscosity and the surface tension of the melt, which accelerates the process of dissolution of the crystals of the mineral part of basalt.

The products of heat treatment at temperature of 1350 °C are a glassy material containing gaseous inclusions. Homogeneous samples of basalt glasses were obtained at 1500 °C.

Basalt glasses crystallizability has been evaluated by means of a complex method based on the results of gradient crystallization and differential scanning calorimetry data. The upper crystallization temperature (liquidus temperature) of the basalt glass is 1275 °C (Table 2). It is rises to 1320 °C by the increase of Al_2O_3 content in the basalt glass composition. Glass synthesized based on boron-containing compositions has the lowest values of crystallization ability. The upper crystallization temperature upon the joint introduction of CaO and B_2O_3 into the composition of glass is reduced by 20 -40 °C, which allows to decrease the fiber molding temperature.

According to DSC data when modifying basalt glass with boron-containing components with an increase of B_2O_3 content in composition, the exo-effects maxima intensity within 800–950 °C is decreased. Endo-effect maximum temperatures in the high temperature area associated with crystalline phases are also reduced (Fig. 1).

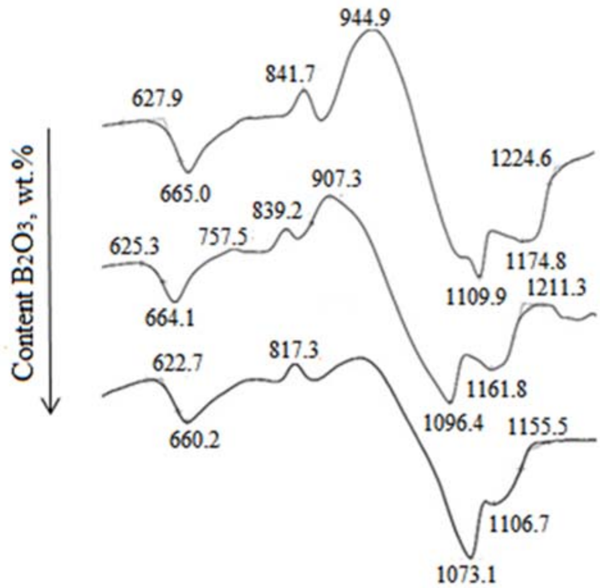


Figure 1. DSC curves of glass (Composition no. 4–6).

According to the data of X-ray diffraction analysis, glass heat treatment products are characterized by the following sequence of crystal phases: magnetite - solid solutions based on diopside-plagioclase with the predominance of anorthite component. During crystallization of basalt glass, the continuity of phase composition of basalt and of basalt glass crystallization products is preserved.

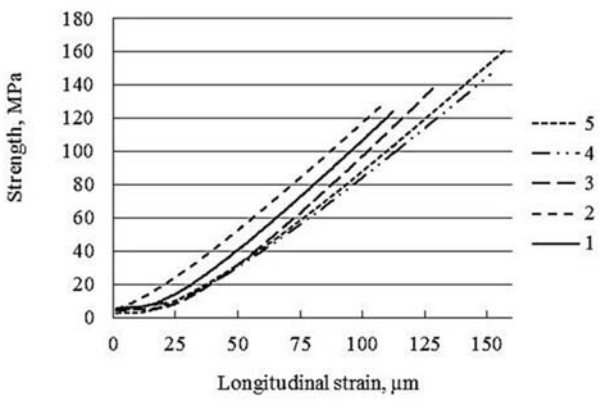
The determination of the glass viscosity in the fiber formation temperature range was carried out by the calculation method according to [7]:

$$\eta = -91{,}22971 + 16{,}06614e^{1{,}25983M\eta}\ (1300\ ^{o}C);$$
$$\eta = -30{,}57462 + 6{,}32023e^{1{,}18491M\eta}\ (1400\ ^{o}C),$$

where $M\eta$ is Viscosity Modulus.

Viscosity indicators of basalt glass increase significantly with the increase of Al_2O_3 content. The lowest levels are achieved by the modification of basalt glass with CaO and B_2O_3 oxides introduced with colemanite. Viscosity and crystallization indicators are the important technological characteristics that determine the temperature regimes for fibre melting and formation. The decrease in the crystallization temperature of basalt glass combined with the reduced viscosity indicators of boron-containing glass will guarantee a decrease in the formation temperature that will result in lower energy consumption and longer service life of the stream feeder assemblies.

The main performance characteristic of continuous fibre is its strength. There is a direct correlation between the strength of the glass and the strength of fibre produced from it. Strain diagrams of basalt glass samples presented in Figure 2.



1 – Basalt glass; 2–5 – Glass of modified compositions
Figure 2. Strain diagrams of basalt glass.

The ultimate flexural strength and, accordingly, the ultimate tensile strength of the glass obtained by melting basalt is 124 MPa. Close values are typical for the glass obtained from basalt-colemanite compositions (sample 2 in strain diagram). The use of basalt-alumina compositions in glass production leads to a significant increase in strength – up to 164 MPa (sample 5 in strain diagram).

The results of the strength values determination specified in Table 2 prove that modification of basalt glass allows to increase the strength by 15–30 %.

In order to determine the strength of the glass under cyclic loads, the samples were subjected to a three-point bending. The load curve had the form of a sinusoidal wave. Figure 3 shows the effect of the load on the number of cycles that the material can withstand until its complete destruction.

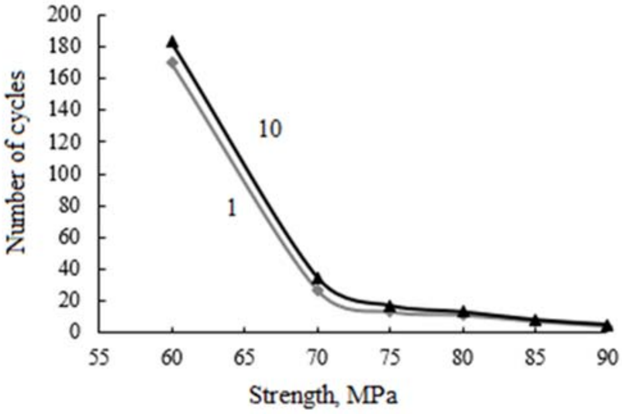


Figure 3. Dependence of the number of cycles on the load (composition 1 and 10).

With the increase of the load applied to the specimens of basalt glass that were modified Al_2O_3, B_2O_3 and CaO from 60 to 70 MPa, the number of loading cycles decreases from 183 to 35. Subsequent increase of the load to 90 MPa results in a monotonic decrease of the loading cycles to 5. For the basalt glass with base composition, when the load increases from 60 to 90 MPa, the number of loading cycles decreases from 170 to 4 MPa. Therefore, both under static and cyclic loads introduction of modifier compound ensures the increase of strength.

Basalt glass alkali resistance indicators based on the mass loss during the exposure to 2 mol/L NaOH solution are 2,4–3,2%. The introduction of modifying additives reduces alkaline resistance insignificantly, and, in case of colemanite, resistance of prototypes increases. Resistance to alkaline environment allows basalt fibres to be used as concrete reinforcement material.

Conclusion

Modified basalt glass was synthesized based on aluminium- and boron-containing basalt-modifier compositions. Disthene-sillimanite concentrate, alumina, colemanite were used as modifying components. Introduction of boron oxide into basalt glass composition intensifies processes of basalt melting, reduces the melt viscosity and the crystallization capacity of the glass. The use of colemanite compositions accelerates the achievement of structural homogeneity of the melt and reduces the crystallization capacity of the glass. At the same time, strength indicators of boron-containing glass are at the level of strength of basic basalt glass. The results of research of elastic -strength properties of basalt glass under static and cyclic loads have confirmed the possibility of increasing the strength of the glass and, as a result, of continuous basalt fibres, through extending the range of chemical composition during the introduction of aluminium-containing components into the composition.

Considering the totality of technological and mechanical properties, introduction of complex aluminum- and boron-containing modifiers is the optimal solution. When basalt-disthene-colemanite compositions were used, samples of basaltic glass with the strength values of 137–148 MPa were obtained. The increase of the strength of basaltic glass will ensure obtaining high-strength basalt fiber, which is highly demanded in production.

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