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RHEOLOGICAL PROPERTIES OF MODIFIED BASALT GLASS

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In this paper the effect of modifying components containing Al_2O_3, B_2O_3, SiO_2 and CaO introduced in various combinations on high and low-temperature viscosity values of basalt glass has been studied. It is shown that the introduction of boron-containing components in compositions with basalt leads to a significant decrease in the viscosity of the basalt melt at all temperature ranges. Influence of modifiers on low-temperature viscosity values of basalt glass correlates with their influence on high-temperature viscosity. Based on experimental values of rheological properties and crystallization ability of modified basalt melts, the modes of basalt fibre production have been determined.

Keywords: basalt melt, continuous fiber, modifier, viscosity, crystallization

РЕОЛОГИЧЕСКИЕ СВОЙСТВА МОДИФИЦИРОВАННОГО БАЗАЛЬТОВОГО СТЕКЛА

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В данной работе исследовано влияние модифицирующих компонентов, содержащих Al_2O_3, B_2O_3, SiO_2 и CaO, вводимых в различных сочетаниях, на значения высоко- и низкотемпературной вязкости базальтового стекла. Показано, что введение борсодержащих компонентов в составы с базальтом приводит к значительному снижению вязкости базальтового расплава во всех диапазонах температур. Влияние модификаторов на значения низкотемпературной вязкости базальтового стекла коррелирует с их влиянием на высокотемпературную вязкость. На основании экспериментальных значений реологических свойств и кристаллизационной способности модифицированных базальтовых расплавов определены режимы получения базальтового волокна.

Ключевые слова: базальтовый расплав, непрерывное волокно, модификатор, вязкость, кристаллизация

O'ZGARITIRILGAN BAZALT SHISHALARNING REOLOGIK XUSUSIYATLARI

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Ushbu maqolada Al_2O_3, B_2O_3, SiO_2 va CaOlarni o'z ichiga olgan komponentlarning turli xil miqdorlarda kiritilgan modifikatorlarni bazalt shishasining yuqori va past haroratli qovushqoqlik qiymatlariga ta'siri o'rganilgan. Ko'rsatilgandek, bazaltli kompozitsiyalarda bor saqlovchi komponentlarning kiritilishi barcha harorat oralig'ida bazalt eritmasining yopishqoqligini sezilarli darajada pasayishiga olib keladi. Modifikatorlarning bazalt shishasining past haroratli qovushqoqlik qiymatlariga ta'siri ularning yuqori haroratli qovushqoqlikka ta'siri bilan bog'liq. Modifikatsiyalangan bazalt eritmalarining reologik xossalari va kristallanish qobiliyatining eksperimental qiymatlari asosida bazalt tolasini ishlab chiqarish usullari aniqlandi.

Kalit so'zlar: bazalt eritmasi, uzluksiz tola, modifikator, yopishqoqlik, kristallanish

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Introduction

In connection with the increasing production of basalt fibre materials, large focus is now being paid to fundamental research into basalt glass and fibres. The interest in basalt fibre is related to a wide range of applications, primarily as a reinforcing material in the production of composites. There are three main kinds of fibres used in modern composites: carbon, polymer and glass fibres. Carbon fibres are highly durable materials with a tensile strength of 4800 MPa and elasticity modulus 230 GPa, but they have a low application temperature and high cost. The strength of polymer fibers is 3000 MPa, the application temperature is 150 °C. Such fibres are subject to degradation of strength when exposed to ultraviolet radiation, they are hygroscopic. The most efficient glass fibre reinforcement materials are high-strength (type S) and basalt fibres. In some cases, basalt fibre is not inferior to high-strength fibre in its mechanical properties, but it is much less expensive [1–4].

However, there are a number of technological problems in production of continuous basalt fibre, related to instability of chemical and mineral composition of basalt and high absorbing capacity of iron-bearing melt [4–7].

One of effective ways to increase performance characteristics of basalt fibres is modification of their composition. Introduction into composition of basalt glass of such components as Al_2O_3, ZrO_2, La_2O_3, MgO and ZnO leads to increase of strength properties and chemical resistance of fibres but increases temperature of its formation [8–14].

The papers [15, 16] present the results of research of glass on the basis of basalt – modifier compositions (disthene, alumina, colemanite, boric acid). The peculiarities of influence of aluminum- and boron-containing components on the melting processes of raw compositions and glass crystallization have been shown. The possibility of increasing the strength of basalt glass by 15 – 25% has been established. The glass synthesized with the use of disthene and colemanite is characterized by the optimum combination of mechanical and technological properties.

Practical implementation of chemical modification of basalt fibres requires information about the rheological properties of the materials. Viscosity determines melting conditions and obtaining of fined homogeneous melt, temperature interval of forming, as well as the upper temperature limit of operation of fibrous materials (thermal resistance).

An experimental study of the temperature dependence of the viscosity of glass-forming melts is a difficult task; therefore, current data on the rheological properties of basalt melts are scarce. The paper [17] presents data on the viscosity of basalt melts obtained 40 years ago according to obsolete methods. According to recent works [10, 18] on basalt melts in the viscosity range of $10–10^3$ Pa·s a significant increase in viscosity with increasing amounts of silicon and aluminum oxides is shown. As the Fe_2O_3 content increases, the activation energy of the viscous flow E_η, respectively the viscosity decreases. The viscosity of basalt fibres as well as the heat resistance increase with the increase of SiO_2 and Al_2O_3 content.

Two mathematical expressions are used to describe the dependence of vitreous melts viscosity on temperature: Arrhenius and Vogel–Fulcher–Tammann equation. During the transition of melts to the glassy state ($10^{13}–10^9$ Pa·s) and at high temperatures the viscosity is calculated according to the Arrhenius equation. The Vogel–Fulcher–Tammann equation is derived from the Arrhenius equation assuming a change in activation energy of the viscous flow and describes viscosity in a wide range of temperatures very well [19, 20]. These equations are used to derive viscosity models for glass-forming melts.

Theoretical and experimental studies of glass-forming liquids have revealed regularities in viscosity-temperature data and this was the basis for the development of viscosity models [21, 22]. The method of glass viscosity calculation based on statistical modelling establishes the limits of applicability according to the content of components [23]. In particular, for glass with high iron oxide content, this model is not adequate. In general, the complex nature of the influence of glass composition and structure on its viscosity practically excludes the development of a universal calculation method for values of this property. Empirical equations for the calculation of viscosity values at a given temperature for basalt melts have been proposed by a number of researchers [24–26].

The aim of this work is to study the rheological properties of basaltic melts and glasses of modified compositions.

Research methods

Basalt andesite was used to obtain basalt glasses, and disthene-sillimanite concentrate (disthene) and colemanite were used as modifiers. The glass synthesis was performed at the maximum temperature of 1500 ± 10 °C for 2 h in a gas furnace (excess air coefficient is 1.08 – 1.13).

The chemical analysis of the have been performed by atomic emission spectroscopy method using a LEA-S500 laser analyzer. In table. 1 shows experimental basalt glasses, which were selected based on the results of a study of strength characteristics [15].

The crystallization ability of glasses was determined by the temperature gradient method in an SP30/13 electric furnace, in which zones with a stable temperature gradient in the range of 800 – 1300 °C are created.

Due to the complex dependence of viscosity on temperature, a range of high, medium and low-temperature viscosity values is distinguished and different measurement methods are used to

Table 1

The chemical composition of experimental glasses

Composition number	Content, 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	11.3	7.98	–	3.94	2.51	1.44	0.96
3	49.09	14.66	12.01	10.63	4.40	4.26	2.37	1.46	1.11
4	50.92	15.29	12.53	9.54	2.29	4.28	2.47	1.52	1.16
5	50.00	18.74	11.58	8.80	2.11	3.96	2.27	1.40	1.10
6	49.44	18.50	11.43	9.15	2.78	3.95	2.24	1.38	1.08
1 – basic composition; modifiers: 2 - disthene; 3 - colemanite; 4 - disthene + colemanite									

Table 2

Experimental and calculated viscosity data

Method	Viscosity, Pa·s, at temperature, °C					
	1200	1250	1300	1350	1400	1450
Viscosity measurements	–	97.5	50.9	27.9	15.4	9.7
Calculated [24]	337.7	118.6	56.5	31.8	19.8	13.3
Calculated [25]	–	–	35.7	–	11.4	–
Calculated [26]	139.16	69.9	36.6	20.0	11.3	6.6

determine the values in these ranges. The high-temperature viscosity of basalt melts in the temperature range of 1250 – 1450 °C was determined using Orton RSV-1600 viscometer. For viscosity measurements, the method of resistance of a rotating platinum rod to a glass melt is used. The measurement was conducted in cooling mode at a rate of 2 °C/min, the rate of rotation of the rod varying from 100 to 0.5 rpm as the melt temperature decreased. The low-temperature viscosity of basalt glasses was determined by dilatometry. The study was carried out using a DIL 402 PC quartz dilatometer (Netzsch). The determination was carried out in the temperature range 20 – 700 °C at a heating rate of 5 °C/min. From the dilatometric curve, a number of characteristic temperatures corresponding to low-temperature viscosity values were determined using an application program.

Results and Discussion

The application of computational methods is the most rational way of determining viscosity as the most important technological property. The chemical composition of basalt glass has been calculated using regression equations developed by the authors [24–26]. The results of the calculation are presented in the Table 2, which also contains the data of experimental determination of the viscosity of basalt melt (composition 1).

Comparison of experimental and calculated data shows that their satisfactory convergence in the temperature range of 1300–1400 °C is achieved using the regression equation proposed by O. S. Tatarentseva et al. [24]:

$$h = 3{,}62(SiO_2)^{3.07}(Al_2O_3)^{-0.16}(CaO)^{-0.4}(FeO+Fe_2O_3)^{1.34}(M_к)^{1.25}(t-1100)^{-2.58},$$

where SiO_2, Al_2O_3, Fe_2O_3+FeO, CaO is content of components, wt.%; M_k is the acidity index.

The use of this equation makes it possible to obtain an estimate of the viscosity of rock melt. A stable glass fibre forming process can be carried out within a certain temperature range determined by the viscosity values (working range of the forming process). At the lower temperature limit, increasing melt viscosity results in a decrease of the melt flow rate and an increase in fibre extension strains which can lead to fibre breakage. According to [1] the temperature of the melt, which has a viscosity of 100 Pa·s, is the general standard for fibre forming. Depending on the staple fibre linear density and a number of technological factors, a viscosity range of $10^{1.5}$ to 10^2 Pa·s corresponds to working forming interval. However, these values refer to the most common borosilicate glass type E.

The Figure 1 shows the temperature dependences of the high-temperature viscosity of basalt glass and E-type glass with B_2O_3 content of 8.0 %. Basalt melt has higher viscosity values. Moreover, a peculiarity of basalt melts is high hardening rate of outer layers at lower hardening rate of inner layers, which is related to high absorption capacity of Fe^{2+} in the near-infrared region of the spectrum.

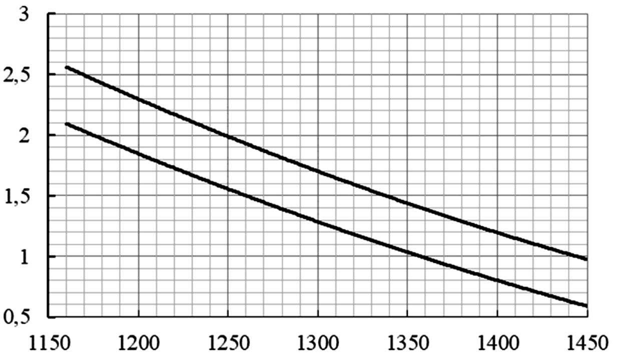


Figure 1. Temperature dependence of basalt (1) and borosilicate (2) glasses viscosity.

During the development of fibre production modes, it is essential to define the technological parameters of forming: the temperature range for fibre formation, the liquidus temperature and the difference between these temperatures, which constitutes the safety range for the formation process. The liquidus temperature, i.e. the temperature at which crystals may emerge from the melt, is defined for multicomponent systems as the upper crystallization temperature [1].

The higher viscosity gradient of basalt glass compared to E-glass as well as the higher liquidus temperature (1270 °C) results in higher working point. In the papers [18, 24, 27, 28] it is shown, that the working viscosity interval of basalt melts during formation of continuous basalt fibres corresponds to values of 10 – 30 Pa·s. However, the working viscosity values of about 10 Pa·s are too low. At lower viscosity values the affinity of the die brim with the melt is improved, which may lead to inflowing to the die margin and temperature disturbances in forming process. When producing staple fibres of different linear density, the temperature range of basic composition during basalt fiber forming is 1300 – 1350 °C. Comparison of experimental data of definition of viscosity of base composition melt with data on technological modes of fiber extension allows considering an optimum interval of values of 30 – 50 Pa·s (lgh is 1.45 – 1.7).

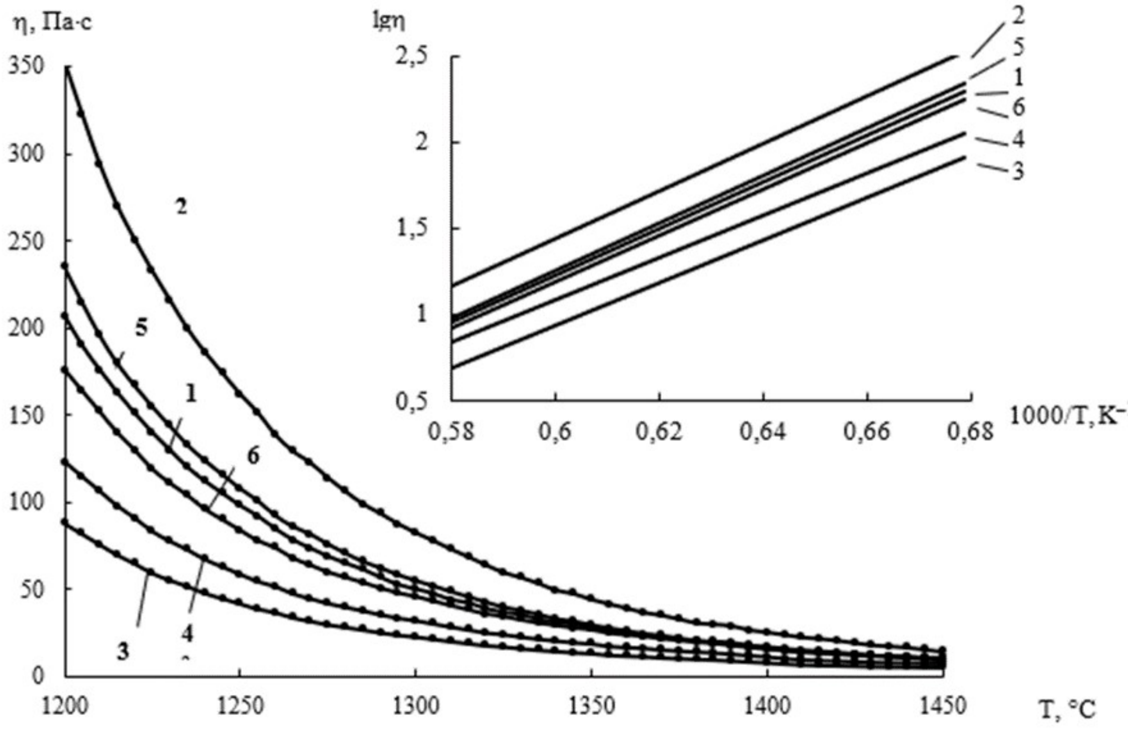
The results of an experimental study of the high-temperature viscosity of basalt melts of modified compositions are shown in Figure 2.

Increasing the Al_2O_3 content in the basalt melt (composition 2) leads to an increase in the viscous flow activation energy (Fig. 1). This is due both to the high strength of the Al-O bond and to the increased degree of cohesion of the structural glassy network due to the embedding of groups $[AlO_4]^{5-}$.

Introduction of B_2O_3 in combination with CaO into basalt glass (composition 3, 4) leads to significant decrease of melt viscosity, which is caused by decrease of bond strength in glass structure. Thus, viscosity of 10 Pa×s for basalt glass is reached at 1440 °C; for glass containing 4.4 wt.% B_2O_3 – at 1385 °C; viscosity 50 Pa·s – at temperatures of 1300 °C and 1240 °C respectively. Decrease in viscosity of boron-containing melts in combination with decrease in liquidus temperature provides decrease in temperature and extension of temperature interval of fibre formation. The safe interval of forming, defined by a difference of temperatures of forming and crystallization, makes not less than 40 °C. It should be noted, that boron oxide lowers a surface tension of the melt, which promotes achievement of structural homogeneity of the melt and stabilizes process of its outflow from the die.

The modification of the basalt glass composition by the introduction of the Al_2O_3, SiO_2, B_2O_3, CaO co-inclusion (composition 5, 6) ensures the rheological properties at the level of the basalt melt viscosity of the basic composition. Thus, the temperature corresponding to viscosity of 50 Pa×s changes within 1295 – 1310 °C. As a result, modification of the composition does not require correction of temperature conditions of fibre formation.

A dilatometric method was used to determine the indicators of low-temperature viscosity. The dilatometric curves were used to determine a number of characteristic temperatures corresponding to low-temperature viscosity values: T_g – glass transition point, corresponding viscosity $10^{12.3}$ Pa×s; annealing points, corresponding viscosity



1–6 is numbers of composition
Figure 2. Temperature dependence of modified glasses viscosity.

Table 3

Data of low-temperature viscosity of basalt glasses

Composition number	Temperature, °C, corresponding to viscosity, lgh				Coefficient of linear thermal expansion, $a \times 10^7$, K^{-1}
	13.5	12.3	12	10	
1	646.2	667.9	679.2	744.0	55.0
2	653.3	684.2	695.0	751.6	51.8
3	614.2	645.3	652.3	725.1	57.8
4	625.3	654.4	660.6	734.8	55.4
5	643.1	662.9	672.5	736.1	53.4
6	647.9	670.5	680.6	743.2	52.0

10^{12} Pa×s and $10^{13.5}$ Pa×s; dilatometric softening point (viscosity is 10^{10} Па×с). The results of definition of the given parameters for the experimental glass are presented in the Table 3.

The glass-transition temperature of experimental glass changes from 645 to 684 ^{o}C, thus it decreases with increasing boron oxide content and increases with increasing of aluminium oxide content. The effect of modifiers on the low-temperature viscosity of basalt glass correlates with their effect on the high-temperature viscosity. The values of glass transition temperature determine the temperature of application of the fibre, i.e. determine its thermal resistance.

Conclusion

Based on experimental values of rheological properties of modified basalt melts, the modes of continuous basalt fibres production have been determined. The optimum working interval of viscosity of basalt melts at formation of continuous basalt fibres, which corresponds to values of 30 – 50 Pa·s, has been determined. Two groups of compositions of modified basalt glass have been selected according to rheological properties. The introduction of boron oxide as a modifying component causes the decrease of viscosity of basalt glass in the whole temperature range. This provides for reduction of temperature and extension of the safety interval of fibre formation. Combined introduction of such modifying components as Al_2O_3, SiO_2, B_2O_3, CaO results in small viscosity variations, i.e. technological parameters of formation are similar to those of basalt glass with a basic composition. The advantage of modified basalt glass is an increase in strength values by 20 – 25%.

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