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(54) Title: COMPOSITION AND METHOD FOR PRODUCING CONTINUOUS BASALT FIBRE

(54) Название изобретения: СОСТАВ И СПОСОБ ПРОИЗВОДСТВА НЕПРЕРЫВНОГО БАЗАЛЬТОВОГО ВОЛОКНА

(57) Abstract: The invention relates to producing continuous organic fibres by stretching it from molten minerals, which can be used for producing heat resistant threads, rovings, cut fibres, fabrics, composite materials and products based thereon. The inventive glass has the following chemical composition in mass%: 15.9-18.10 Al_2O_3, 0.75-1.2 TiO_2, 7.51-9.53 Fe_2O_3, 6.41-8.95 CaO, 2.5-6.4 MgO, 1.6-2.72 K_2O, 3.3-4.1 Na_2O, 0.23-0.5 P_2O_5, 0.02-0.15 SO_3, 0.12-0.21 MnO, 0.05-0.19 BaO, impurities up to 1.0, the rest being SiO2. The inventive method consists in loading a ground composition in a melting furnace, in melting said composition, in homogenising a melt, in consequently stabilising the melt in the melting furnace feeder, in drawing and oiling fibre and in winding it on a spool. Prior to loading, the composition is hold in an alkali solution for 15-20 minutes, is washed with flowing water for 20-30 minutes and is dried. After having been washed with flowing water and dried the composition is loaded in the melting furnace.

(57) Реферат: Изобретение относится к технологии производства непрерывных органических волокон из расплавленных минералов вытягиванием, которые могут использоваться для получения термостойких нитей, ровингов, рубленных волокон, тканей, композиционных материалов и изделий на их основе. Стекло имеет следующий состав, масс.%: Al_2O_3 - 15.90-18.10, TiO_2 - 0.75-1.20, Fe_2O_3 - 7.51-9.53, CaO - 6.41- 8.95, MgO - 2.5-6.40, K_2O - 1.60-2,72, Na_2O - 3.30-4.10, P2O5 - 0.23-0.50, SO_3 - 0.02- 0.15, MnO - 0.12-0.21, BaO - 0.05-0.19, примесей - до 1.00, SiO_2 - остальное. Способ включает операции загрузки измельченного состава в плавильную печь, его плавление, гомогенизацию расплава, последующую стабилизацию расплава в фидере плавильной печи, вытягивание волокна, его замасливание и наматывание на бобину. Перед загрузкой состав выдерживают в растворе щелочи в течение 15-20 минут, промывают проточной водой в течение 20-30 минут и высушивают. После промывания проточной водой и высушивания состав загружают в плавильную печь.

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COMPOSITION AND METHOD FOR PRODUCING CONTINUOUS BASALT FIBRE.

The proposed inventions pertain to technology of continuous inorganic fibers manufacturing, preferably, by way of drawing from melted minerals. Such continuous inorganic fibers may be used in production of heat-resistant threads, rovings, cut fibers, fabrics, composition materials and products based on such materials.

Production of fibrous materials based on mineral, glass and other fibers is intensively developing in CIS and other countries. Nevertheless, the production volume increase is restrained by growing technical demands to such materials and also by the deficit of raw materials.

Meeting the increasing needs in fibrous materials is predetermined by drastic increase of their quality. With a view to the above, in CIS prevailing production type is production of basalt fibers and materials based on such fibers with rocks (basalt, gabbro-diabases, porphyrites, etc.) used as one-component raw material.

Using basalt fibers as a raw material enables production of materials replacing asbestos, metal, wood, etc.

The most similar to the proposed composition in terms of a number of essential features is the composition for production of continuous basalt fiber containing the mixture of silicon (SiO_2), aluminum (Al_2O_3), titan (TiO_2), iron (Fe_2O_3 and FeO), calcium (CaO), magnesium (MgO), manganese (MnO) oxides and also admixtures (RF Patent No. 02118300, IPC 6 C03B 37/02, 1998). Average elements of the initial composition are presented in Table 1.

Table 1

Comp. No.	Average elements of the initial composition									
	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe	P
1	6.325	1.970	17.833	55.903	4.558	4.672	1.582	0.160	6.997	0.000
2	5.083	7.932	14.127	46.154	2.320	4.697	1.343	0.396	16.461	1.512
3	5.877	2.773	17.493	53.716	3.923	4.867	1.299	0.098	8.276	1.680
4	4.357	3.187	17.660	52.501	3.927	5.515	1.701	0.155	8.541	1.953
5	4.404	3.470	15.324	51.606	2.810	7.681	1.852	0.185	9.223	2.944

The drawback of the described composition is insufficient strength of continuous fibers produced. This is due to high upper limit of crystallization of the composition (1245 to 1290°C), which prevents stable process of continuous basalt fiber formation.

In terms of a number of essential features, the closest method to the proposed one is the method of continuous basalt fibers production comprising operations of the crushed composition loading into the melting furnace, melting, melt homogenization, subsequent stabilization of the melt in the melting furnace feeder, drawing, lubrication and winding the fiber onto the reel (RF Patent No. 02118300, IPC 6 C03B 37/02, 1998).

The drawback of the described method is insufficient strength and chemical stability of continuous fibers produced in this way, which is due to narrow temperature range of fibers forming. Difference between fiber forming temperature and upper crystallization limit is 70 to 100°C on the average, which causes instability of continuous fiber drawing due to primary crystallization occurring is such temperature range. Such primary crystallization causes thread breakages. As seen from the practice, the temperature of forming should be at least 110°C above upper crystallization limit.

The proposed inventions aim at providing the means for obtaining stronger and chemically more stable fibers by way of creating the conditions for decreasing the number of defects on the fiber surfaces.

This objective is attained by the proposed composition for production of continuous basalt fiber containing the mixture of silicon (SiO_2), aluminum (Al_2O_3), titan (TiO_2), iron (Fe_2O_3 and FeO), calcium (CaO), magnesium (MgO), manganese (MnO) oxides and admixtures and also, *according to the present invention*, this composition further contains potassium (K_2O), sodium (Na_2O), barium (BaO) oxides with the following components ratio (in mass %):

Al_2O_3	15.90 – 18.10
TiO_2	0.75 – 1.20
Fe_2O_3 + FeO	7.51 – 9.53
CaO	6.41 – 8.95
MgO	2.50 – 6.40
K_2O	1.60 – 2.72
Na_2O	3.30 – 4.10
P_2O_5	0.23 – 0.50
SO_3	0.02 – 0.15
MnO	0.12 – 0.21
BaO	0.05 – 0.19
admixtures,	up to 1.00
SiO_2	the rest.

The objective is also attained by the proposed method, which, like the known method of continuous basalt fibers production, comprises operations of the crushed composition loading into the melting furnace, melting, melt homogenization, subsequent stabilization of the melt in the melting furnace feeder, drawing, lubrication and winding the fiber onto the reel, and, *according to the invention,* the composition is held in alkaline solution during 15 to 20 minutes, then washed by running water during 20 to 30 minutes and loaded into the melting furnace after such washing.

The feature of the proposed method is the use of sodium hydroxide (NaOH) and potassium hydroxide (KOH) solution with (0.1...0.5) N concentration as the alkaline solution.

The invention idea is in creation of conditions for obtaining melt with pH 5...7. This is because our experiments show that such melt pH ensures producing of homogenous chemical composition. Acidic melt components react with alkaline components and give chemically neutral melt. Gas microbubbles do not appear in such relatively neutral melt during cooling, unlike conventional rock melts. Thus, the number of surface defects on the fibers produced is much less, therefore, diameter of elementary fibers may be smaller without compromising the strength. Adding alkali metals oxides to the known composition of the furnace charge in the above amount promotes producing of chemically neutral melt composition. Thus, with K_2O and Na_2O in amount over 4.1 mass % and less than 1.6 mass % the melt acidity is changed causing chemical reactions in the melt and microbubbles generation. BaO presence in the melt in amount of 0.05 to 0.19 mass % as well as other admixtures presence increases melt diathermancy, thus forming interval becomes larger and conditions of fiber forming are improved, surface defects become less, and conditions for compressed surface layer are created, while such compressed layer prevents stretching forces appearance under bending loads. The latter is attained by changing the composition of the surface layer by way of substituting alkali ions with a big radius by ions having smaller radius and vice-versa. The oxides listed among the admixtures are present in the composition of the fiber being strengthened for ion exchange purposes. In addition, for example, presence of zinc oxide (ZnO) in the proposed composition as an admixture results in formation of acid resistant solid solution together with aluminum oxide (Al_2O_3). Acid resistance is also improved by phosphorus oxides and other admixtures, i.e. oxides of the elements of the III and V groups in Mendeleev's Periodic Table of the Elements. By experimental way the authors have found that the substances with structures similar to precipitates structures are formed on the fibers obtained. This is occurring in case of treating the furnace charge of the proposed composition by alkaline solution prior to its loading to the melting furnace. Such structures essentially increase the fibers surface strength.

Also, by way of experiments, the authors have found the processing mode parameters for the proposed composition, beginning from its loading to the

melting furnace until continuous basalt fibers production. Thus, in case of holding the proposed composition (furnace charge) in alkaline solution for less than 15 minutes, the effect of the proposed method is not practically visible. Holding the furnace charge in alkaline solution for more than 20 minutes is not justified economically.

Furnace charge is washed in the running water during 20 to 30 minutes, because this time is enough to remove the alkaline solution which otherwise may cause corrosion of the melting furnace walls.

The proposed composition contains the following admixtures (mass %):

Cr_2O_3	0.010 – 0.0315
Co_2O_3	0.0005 – 0.0047
NiO	0.0079 – 0.0091
CuO	0.0065 – 0.0087
ZnO	0.0083 – 0.0159
Ga_2O_3	0.0029 – 0.0051
Rb_2O	0.0049 – 0.0095
SrO	0.0585 – 0.0923
ZrO_2	0.0127 – 0.0173
Nb_2O_5	0.0011 – 0.0019
V_2O_5	0.029 – 0.043,
F-containing compounds	0.06 – 0.11
Cl-containing compounds	0.0270 – 0.0520,

their amount practically has no effect on the quantity of structures similar to precipitates appearing on the fiber surfaces.

Sodium hydroxide (NaOH) and potassium hydroxide (KOH) solutions have approximately the same chemical characteristics. But the furnace charge material structure is not homogenous. Thus, some of its elements react more actively with sodium hydroxide (NaOH), while others react more actively with potassium hydroxide (KOH). The amounts of sodium hydroxide (NaOH) and potassium hydroxide (KOH) in solution are approximately the same. Sodium hydroxide

(NaOH) and potassium hydroxide (KOH) solution concentration is (0.1...0.5)N. Using more concentrated solutions is not economically justified.

Implementation of the proposed inventions results in producing of the stronger continuous basalt fiber. The continuous fibers so obtained also possess higher heat and acid resistance.

The method is realized as follows.

The above composition, ground to dispersion level of 1.0...5.0 mm, was charged into a tank filled with sodium hydroxide (NaOH) and potassium hydroxide (KOH) solution with concentration 0.5 N and the temperature +20°...+60°C. Such ground composition was held in the solution during 15 to 20 minutes under continuous agitation. Then the solution was poured out and the ground charge was washed by running water during 30 minutes. The charge was then dried by air forced through the charge. Treated and dried charge was loaded into the melting furnace with temperature set at 1400–2000°C. Melt was produced from the charge. This melt was left to stay for some time for homogenization. Homogenized melt was fed to fiber forming zone, which is a feeder and spinnerets. The temperature in the forming zone was maintained at the level exceeding crystallization temperature of the melt produced. The melt came out of the spinnerets in the form of drops forming cones, which separated from the spinnerets after some increase in mass and formed the fibers. Fibers drawing was performed without stops and delays. To prevent mutual friction and adhesion of the fibers, they were lubricated on the roller lubricating unit. Continuous fiber forming was stable.

Table 2 shows that the upper crystallization limit (T_{ucl}) was lower for the proposed composition compared to the prototype, while fiber forming interval was larger.

Also, experimental evaluation of chemical resistance of the fibers produced using hydrochloric acid (HCl) solution proved that these fibers possess higher acid resistance than the fibers produced according to prototype method.

The continuous fibers chemical resistance to acid and alkali solutions was determined by measuring the mass loss from the 5000 sq.cm surface after 3 hours of boiling (Table 3).

Table 2

Melt and fibers technological properties	Composition of fiber	
	produced according to the proposed method	produced according to the prototype method
Upper crystallization limit temperature, T_{ucl}, °C	1210 – 1230	1240 – 1290
Forming temperature interval, , °C	1320 – 1430	1350 – 1430
Elementary fiber average diameter, μm	7 ± 2	8.5
Tensile strength, MPa	2250 – 3200	2240 – 3110

Table 3

Medium	Resistance of fibers produced from the proposed composition, %	Resistance of fibers produced from the prototype composition, %
2N HCL solution	97.1	91.0
2N NaOH solution	98.2	96.8
$Ca(OH)_2$	99.7	-----

Table 3 shows that continuous fibers produced from the proposed composition and by the proposed method possess high resistance to both acids and saturated alkaline solution ($Ca(OH)_2$). Therefore they may be widely used, for example, in filter materials, composite reinforcing fillers, etc. resistant to aggressive media.

Information sources:

1. RU 2018491 C1, 28.02.79

2. SU 649670 A, 03.03.79

CLAIMS

1. Method of continuous basalt fiber production from a composition containing the mixture of silicon (SiO_2), aluminum (Al_2O_3), titan (TiO_2), iron (Fe_2O_3 and FeO), calcium (CaO), magnesium (MgO), manganese (MnO) oxides and admixtures, *wherein* this composition further contains potassium (K_2O), sodium (Na_2O), barium (BaO) oxides with the following components ratio (in mass %):

Al_2O_3	15.90 – 18.10
TiO_2	0.75 – 1.20
Fe_2O_3 + FeO	7.51 – 9.53
CaO	6.41 – 8.95
MgO	2.50 – 6.40
K_2O	1.60 – 2.72
Na_2O	3.30 – 4.10
P_2O_5	0.23 – 0.50
SO_3	0.02 – 0.15
MnO	0.12 – 0.21
BaO	0.05 – 0.19
admixtures,	up to 1.00
SiO_2	the rest,

the method comprising operations of the crushed composition loading into the melting furnace, melting, melt homogenization, subsequent stabilization of the melt in the melting furnace feeder, drawing, lubrication and winding the fiber onto the reel, *wherein* the composition is held in alkaline solution during 15 to 20 minutes, then washed by running water during 20 to 30 minutes, dried and loaded into the melting furnace after such washing and drying.

2. Method of continuous basalt fiber production according to claim 1, *wherein* sodium hydroxide (NaOH) and potassium hydroxide (KOH) solution with (0.1...0.5) N concentration is used as the alkaline solution.