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Improvement of strength characteristics of quartz ceramics

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The paper deals with one of the methods of increasing the strength of quartz ceramics, i.e. introduction of a finely dispersed fibrous aluminosilicate additive into the material. The additive is introduced into the slip of finely ground quartz glass cullet in the amount of 1–3 weight % and promotes improvement of the uniformity of the slip suspension, which reduces its tendency to subsidence. Introduction of the above additive also allows increasing the bending strength of the semi-finished product and sintered material 1.8–2.1 times. Furthermore, the introduction of fibers into quartz ceramics leads to increase in the particles' packing density during formation of the ceramic body structure, which is manifested in the reduction of water absorption indices by an average of 10 %.

Keywords: quartz ceramics, quartz glass cullet, aluminosilicate fibers, slip, glass phase, cristobalite, firing, water absorption, mechanical strength.

Рассмотрен один из способов повышения прочности кварцевой керамики, который состоит во введении в состав материала тонкодисперсной волокнистой алюмосиликатной добавки. Добавка вводится в шликер тонкомолотого боя кварцевого стекла в количестве 1–3 мас.% и способствует повышению однородности шликерной суспензии, снижению ее склонности к оседанию. Введение указанной добавки также позволяет повысить прочность полуфабриката и спеченного материала на изгиб в 1,8–2,1 раз. Кроме того, введение волокон в состав кварцевой керамики приводит к повышению плотности упаковки частиц при формировании структуры черепка, что проявляется в снижении показателей водопоглощения в среднем на 10 %.

Підвищення міцності кварцової кераміки. *О.С.Хоменко, О.В.Зайчук, О.В.Карасик, В.Д.Івченко, Н.М.Срібняк, Б.М.Даценко.*

Розглянуто один із способів підвищення міцності кварцової кераміки, який полягає у введенні до складу матеріалу тонкодисперсної волокнистої алюмосилікатної добавки. Добавка вводиться у шлікер тонкомолотого бою кварцового скла у кількості 1–3 мас.% і сприяє підвищенню однорідності шлікерної суспензії, зниженню її схильності до осідання. Введення зазначеної добавки також дозволяє підвищити міцність напівфабрикату і спеченого матеріалу на вигин в 1,8–2,1 разів. Крім того, додавання волокон до складу кварцової кераміки призводить до підвищення щільності упаковки частинок при формуванні структури черепка, що проявляється у зниженні показників водопоглинання у середньому на 10 %.

1. Introduction

Quartz ceramics widely used in the aircraft industry and other critical areas represents rather specific material, both in terms of its valuable properties and manufacturing technology. Such ceramics is characterized by high thermal resistance, stability of dielectric parameters in a wide temperature range, as well as radio-transparent characteristics [1]. At the same time, the strength of quartz ceramics is rather low because of the difficulty to obtain the dense structure of products during sintering [2].

The difficulties of sintering of quartz ceramics lie in the fact that at the temperatures above 1200°C, silica-containing raw materials are subject to intensive crystallization with the formation of cristobalite. Cristobalite, in its turn, changes its volume during the process of polymorphic transformations; this causes loosening of the structure and sharp decrease in the strength of the sintered material. Therefore, many research papers deal with studying of various ways to reduce the tendency to crystallization of the material under firing quartz ceramics and to form its dense structure.

The effect of gas atmosphere and temperature of quartz ceramics firing on its phase composition and physico-technical parameters is considered in [3]. It is shown that sintering of quartz ceramics in the air results in the intensive formation of a cristobalite phase even at the temperature of 1250°C, leading to the growth of the coefficient of thermal expansion of the material (α) to $(64.3-96.6)\cdot 10^{-7}$ deg^{-1}; it negatively affects the ability of the glass ceramics to resist the thermal stresses. The practicability of the heat treatment of quartz ceramics in the reducing environment is established; this makes it possible to shift the temperature range of intensive crystallization of cristobalite above 1350°C. This technique allows you to obtain the material with rather high thermo-physical properties (TCLE (α) = $(13.7-19.4)\cdot 10^{-7}$ deg^{-1}). In this case, mechanical compressive strength of the material is 72.3–104.1 MPa. However, the creation and continuous monitoring of the reducing environment cause certain technical difficulties in the implementation of this method.

Process conditions for obtaining quartz ceramics from the synthetic powder of silicon dioxide produced with the use of a sol-gel method were developed [4]. In this case, the presence of traces of cristobalite reducing the mechanical strength of the material is observed in the samples after firing at the temperature of 1250°C. In this connection, the firing at lower temperatures is recommended. However, this production method is unacceptable because of the need to use a large amount of nano-sized silicon dioxide which increases the cost of the final product significantly.

The method described in [5] appears more practical: physico-technical characteristics of quartz ceramics are increased after introducing a modifying additive of nano-sized silica into the charge with the quartz tube cullet; the additive is obtained by a sol-gel method on the basis of ethyl silicate or tetraethoxysilane. The amount of the additive is 10 weight %. The samples containing an activator feature 40–45 % less water absorption compared to the samples without the activator, but the mechanical compressive strength increases 1.2–1.3 times. Besides, this activator prevents the formation of an undesirable cristobalite phase in quartz ceramics. This method can be applicable perfectly well in the production environment due to small quantities of the required modifying additive; however, industrial production of silica in this way has not been set up at the moment.

The work [6] is focused on the purity of quartz-containing raw materials used in the production of quartz ceramics. For example, for the production of rocket fairings it is recommended to use transparent quartz glass with the content of SiO_2 of min. 99.9 % as the basic material. Optimal properties of the material for quartz fairings (porosity 9–10 %, ultimate bending strength 50–60 MPa) are achieved at the firing temperature of 1250–1280°C and linear contraction within 1.0–1.2 %. However, given the limited resources of high-purity quartz glass and a higher temperature of firing of the products, this method is not economically feasible as well.

Quartz ceramics with a uniform distribution of the $BaTiO_3$ compound up to 8 wt.% in its structure is proposed in [7]. The material is produced by molding of the powder mixture followed by sintering. In addition to provision of the basic physical properties of the quartz ceramics, attention is paid to increasing the material's ability to absorb electromagnetic waves; the reflecting power of the electromagnetic wave of the developed material might reach 7.0 dB with the sample thickness of 6 mm only.

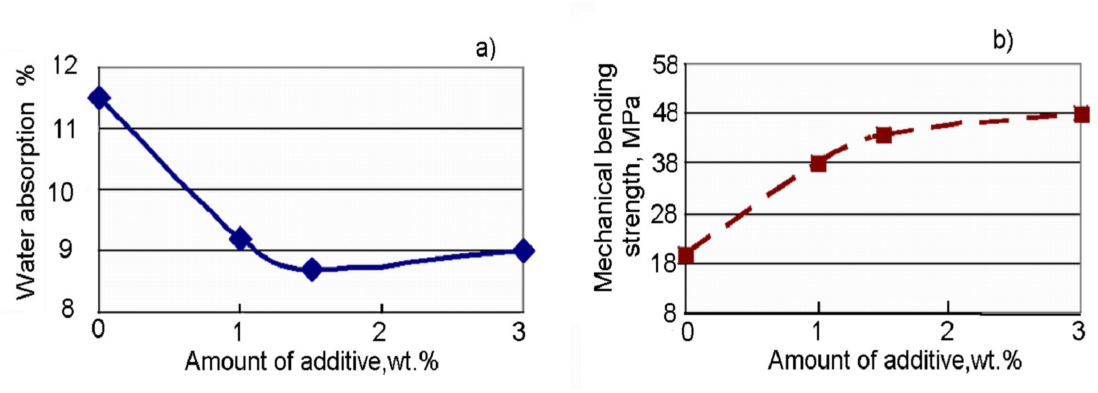


Fig. 1. Physical-technical properties of experimental samples.

In order to reduce porosity and to increase the strength of quartz ceramics, the researchers [8–10] proposed the use of an additional operation to modify its structure by impregnating semi-finished products or fired products with various organosilicon binders. Implementation of such methods is associated with additional resource and energy demands, but does not always allow achieving high performance of quartz ceramics.

Thus, no valid method suitable for efficient implementation in the production environment has been found for increasing the strength characteristics of quartz ceramics; this indicates the relevance of research in this direction.

2. Experimental

In view of the aforesaid, the objective of this work is to study the possibility of hardening of quartz ceramics by modifying its structure with a finely dispersed fibrous additive of aluminosilicate composition.

To achieve this objective, it is necessary to study the rheological and processing characteristics of slips upon introduction of the finely dispersed fibrous additive into their composition, as well as its effect on the formation of microstructure, phase composition and properties of quartz ceramics.

As the basic raw material for research, quartz glass cullet is taken.

Standard research methods [11], such as determination of the moisture content of ceramic slips by weight loss, measurement of particle size distribution using the sieve method, and water absorption of the fired samples by the method of hydrostatic weighing are used in this study. Slip casting ability was evaluated with the use of the Ford Cup by the time of flow of 100 ml of suspension through a hole of 6 mm in diameter in the cup. Mechanical bending strength of the fired samples was measured using a hydraulic press at the constant rate of load rise (0.05±0.01) MPa/s until the samples were completely destroyed; the measurement error was equal up to 5 %.

Phase composition of the fired samples was studied by X-ray diffraction analysis [12] on the DRON-3M instrument using an X-ray tube with a copper anticathode. Volume resistivity of the experimental samples was determined by a tera-ohmmeter E6-13A. For studying the microstructure of the fired samples, a scanning electron microscope "REM-106-I" with a 1000–3000x magnification was used.

Ceramic fibers have been widely used as high-temperature heat insulation materials in recent decades [13, 14]. The use of ceramic fibers of small (about 10–20 μm) diameter reached the new stage of development in the domain of reinforcement of ceramic and metal composites with high operating temperatures [15].

Quartz ceramics, in spite of many advantages thereof, represents a rather brittle material. As a result, its bending strength is in most cases unsatisfactory. Considering all the advantages of modern fibers of aluminosilicate composition [16], namely lightness, wear resistance, strength, resistance to oxidation and thermal shock etc., this work deals with the effect of these fibers on the change in physical and ceramic properties of quartz ceramics.

Finely dispersed fibrous material with the prevailing size of fibers of 0.5–2 mm was chosen. Technical characteristics of the fibers are given in Table 1. The modifying additive was introduced into the composition of quartz ceramics in the amount of 1–3 wt.%.

Slips were prepared by fine wet grinding of quartz class cullet in the ball mill. Grinding equipment was charged in the ratio: "quartz glass : grinding media : water" in

Table 1. Technical characteristic of aluminosilicate fiber

Name of the characteristic	Index
Operating temperature, °C	
— maximum temperature	1269–1300
— working temperature	1100–1200
Density, kg/m^3	128
Ultimate tensile strength (128 kg/m^3), MPa	≥0.06
Chemical composition:	
— SiO_2	51–55
— Al_2O_3	45–49

the amounts of 1:2.5:0.15. Grinding of quartz glass was carried out in one step until the sieve No.0063 residue percentage of 0.4 % was obtained. Further, 1–3 % (in relation to dry substance) of the modifying fibrous additive was introduced into the slips with the subsequent thorough mixing. Suspensions obtained as a result were stabilized for 6 h, after which their rheological and processing properties were measured (Table 2). Then, by means of casting into gypsum molds, tile samples of 5×3×0.8 cm^3 in size were made of the slips to determine physico-technical properties.

From the results obtained it follows that the introduction of a fibrous additive increases the normal working moisture level of the slip from 30 to 35 % due to the fact that the fibrous material is hygroscopic and absorbs water. Consequently, more water is required to obtain a free-flowing state of the slip. Introduction of additives of up to 3 wt.% also leads to increase in the time of flow of the slip from 17 to 25 s; this, in the case of its maximum amount, might cause difficulties in the process of suspension casting into the gypsum mold and discharge of its residue after composing of the product wall. Since the indicators of fluidity of 18–22 s [11] are commonly believed the most optimal, the amount of introduced modifying additive in this case should be limited to 1.5 wt.%.

At the same time, a positive effect of the modifying with fibrous additive on the properties of slips is observed. The fact is that the particles of the main component of the material, i.e. quartz glass, even after very fine grinding in the aqueous medium, tend to settling; this complicates the processing operations with the slip [2]. Furthermore, with fine grinding of quartz glass cullet it is difficult to achieve a poly-disperse slip composition which would ensure compacting of grains during molding. Introduction of aluminosilicate fiber in the amount of 1.0–1.5 wt.% allows us to reduce the tendency of slip to settling and to achieve the satisfactory rheological and processing properties.

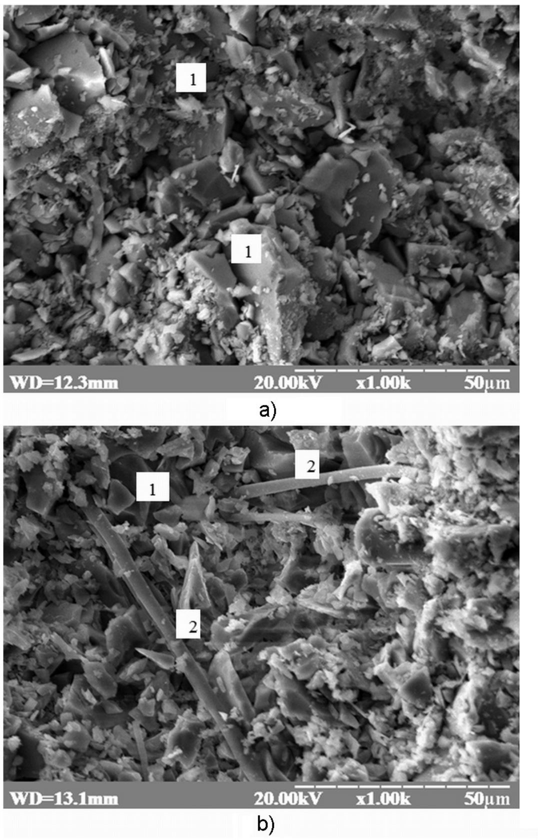
Experimental samples were dried at the temperature of 100–120°C during 4 h in the dry chamber. Firing was carried out in the laboratory silit furnace at the temperature of 1200°C with holding for 1 h. Physical-technical properties of the experimental samples are given in Table 1.

3. Results and discussion

The data presented show a significant reduction in water absorption of the sintered samples (from 11.5 to 8.7 %) and an increase in mechanical bending strength (from 20 to 44 MPa) upon introduction of the additive in the amount of 1.0–1.5 weight %. These changes occur due to the provision of better homogeneity of the semi-finished product during molding and creation of a compact structure owing to the uniform distribution of the particles of the fibrous additives between the larger particles of quartz glass. In addition, the fibers have the "reinforcing" effect on the structure of the material (Fig. 2).

Table 2. Rheological and processing properties of slips under study

Parameter name	Numbers of compositions			
	0 (basic)	1	2	3
Content of fibrous additives, wt.%	–	1.0	1.5	3.0
Slip moisture content, %	30	31	32	35
Fineness of grinding of quartz glass cullet by the residue on sieve No.0063, %	0.4			
Slip casting ability (Ford cup), s	17	18	22	25
Time of composing a wall of 4 mm thick on the surface of gypsum mold, min	13	19	23	29



a)

b)

Fig. 2. Microstructure of samples of quartz ceramics without additive (a) and with modifying fibrous additive in the amount of 1.5 wt.% (b): 1 — grains of finely ground quartz glass cullet, 2 — fibers of modifying additive.

Table 3. Properties of experimental samples

Sample No.	Electrical resistance index (300°C), ρ_{qu}, Ohm·m	Temperature coefficient of linear expansion, $\alpha_{0-500^\circ C}$, $^\circ C^{-1}$
0	$3.66 \cdot 10^9$	$8.3 \cdot 10^{-7}$
1	$3.68 \cdot 10^9$	$8.0 \cdot 10^{-7}$
2	$3.70 \cdot 10^9$	$8.0 \cdot 10^{-7}$
3	$3.75 \cdot 10^9$	$7.8 \cdot 10^{-7}$

The increase in water absorption with the introduction of a larger amount of the additive and the slowdown in the development of the bending strength of the samples can be explained by the decrease in the quartz ceramics' sintering intensity, since the chemical composition of the fibers is represented by refractory Al_2O_3 and SiO_2 components.

X-ray patterns of the experimental materials (Fig. 3) show an amorphous ring which indicates the absence of a significant amount of crystalline phases. The crystalline phase of α-cristobalite (with a maximum diffraction line corresponding to an interplanar distance of 4.02 Å), which is the most harmful from the point of view of loosening the structure and destruction of the material, is present in small amounts in quartz ceramics without a modifying additive.

Indices of thermal expansion and electrophysical properties of the samples of quartz ceramics under study are presented in Table 3.

One of advantages of quartz ceramics is its low expansion under thermal loads [1]. This property is due to the main raw material — quartz glass; however, formation of the cristobalite phase in the material, as a rule, leads to sharp increase in the thermal expansion index. If no cristobalite phase is formed, the index of thermal expansion does not increase. The obtained results correlate well with the data of the X-ray diffraction analysis.

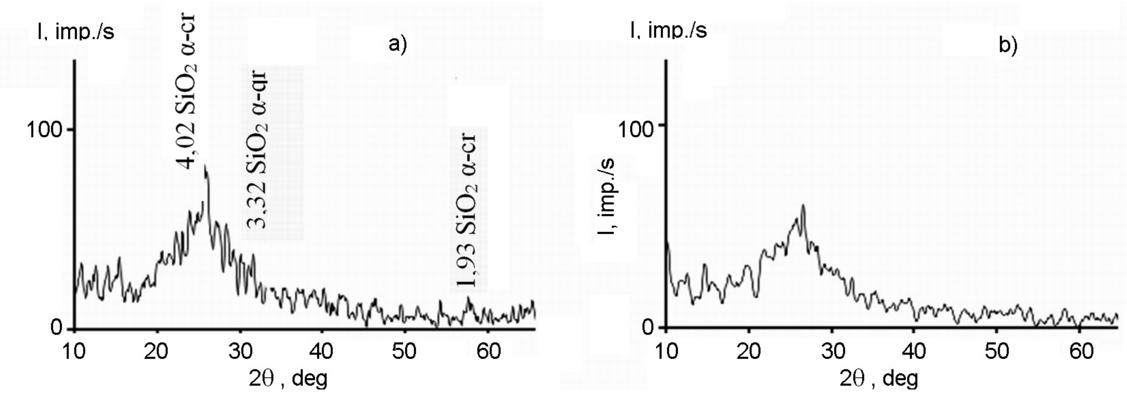


Fig. 3. X-ray patterns of quartz ceramics without additive (a) and with modifying additive in the amount of 1.5 wt.% (b): cr — cristobalite, qr — quartz.

Quartz ceramics refers to radio-transparent materials (dielectrics), which do not change the amplitude of the transmitted electromagnetic wave and do not cause a chaotic change in its phase [17]. The transparency of these materials for radio-waves means that in the range of operating temperatures they have very low dielectric losses and actually do not reflect radio- waves. It can be seen from the table above that the volume resistivity index for the samples correlates with the same index for other researchers' quartz ceramics ($\rho_{qu} = 10^9$ Ohm·m [1]). Introduction of the modifying fibrous additive has practically no effect on this index. Both materials belong to the class of dielectrics for which $\rho_{diel} > 10^8$ Ohm·m [18].

4. Conclusions

The method for hardening of quartz ceramics by modification of its structure with a finely dispersed fibrous additive of the aluminosilicate composition is developed in this work. The optimal amount of the additive introduced into the slip of finely ground quartz glass cullet is 1.0–1.5 wt.%; this helps to improve rheological properties of the slip and to reinforce the structure of quartz ceramics after firing. This allows a 1.8–2.1 times increase in the bending strength of the material. Furthermore, the introduction of fibers into quartz ceramics leads to an increase in the particles' packing density during formation of the ceramic body structure, which is manifested in a decrease of water absorption indices by an average of 10 %.

The phase composition of the developed material is characterized by the absence of cristobalite phase in the structure of the sintered ceramic body. This ensures low thermal expansion of the material when heated ($\alpha_{0-500^{\circ}C} = 7.8 \cdot 10^{-7}\,^{\circ}C^{-1}$), as well as high dielectric properties ($\rho = 3.75 \cdot 10^9$ Ohm·m).

The proposed method of hardening of quartz ceramics can be used in the manufacture of general-purpose products, in particular, elements of rocket and space equipment, quartz crucibles for metal smelting, refractory materials, components of capsules of nuclear reactors, reflectors for quartz heat-emitting lamps, reflectors of optical telescopes, radio-telescopes etc.

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