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Impact of kaolin addition on properties of quartz ceramics

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This paper presents one of methods of the quartz ceramics technological and physical-and-mechanical properties improvement by introduction of kaolin additive to its composition. Additive was added to slip prepared of the scrap quartz tubes; additive amount made 5, 10 and 15 wt. %. This results in observed improvement of rheological-and-processing characteristics for all slips, of which major one is reduction of slip tendency for sedimentation. In addition, the introduction of additive enhances compression strength of burned quartz material due to formation of the closely packed structure as compared with material without additive, which results in the material compression strength increase from 51 to 72 MPa.

Keywords: quartz ceramics, slip, fluidity, kaolin, cristobalite, burning, water absorption capacity, mechanical strength.

Рассмотрен один из способов улучшения технологических и физико-механических свойств кварцевой керамики путем введения в ее состав добавки каолина. Добавку вводили в шликер, приготовленный из боя кварцевых трубок, количество добавки составляло 5, 10 и 15 масс.%. При этом для всех шликеров наблюдается улучшение реолого-технологических характеристик, главная из которых — снижение склонности шликера к оседанию. Кроме того, введение добавки увеличивает прочность кварцевого материала на сжатие в обожженном состоянии за счет создания структуры, имеющей более плотную упаковку по сравнению с материалом без добавки, что приводит к повышению механической прочности материала на сжатие от 51 до 72 МПа.

Вплив добавки каоліну на властивості кварцової кераміки. *О.С.Хоменко, О.В.Карасик, В.І.Голеус*

Розглянуто один із способів покращення технологічних та фізико-механічних властивостей кварцової кераміки шляхом введення до її складу добавки каоліну. Добавку вводили в шлікер, приготовлений з бою кварцових трубок, кількість добавки становила 5, 10 та 15 мас.%. При цьому для всіх шлікерів спостерігається покращення реолого-технологічних характеристик, головна з яких — зниження схильності шлікеру до осадження. Окрім того, введення добавки збільшує міцність кварцового матеріалу на стискання у випаленому стані за рахунок створення структури, що має більш щільну упаковку у порівнянні з матеріалом без добавки, що призводить до підвищення механічної міцності матеріалу на стискання від 51 до 72 МПа.

1. Introduction

Quartz ceramics products are commonly used in various areas of science and technology. For example, quartz ceramics is used as refractory materials of both general and special purpose, for manufacture of rocket and space equipment including radiotransparent aircraft radomes, and in the nuclear power industry and other areas with extremely severe operating conditions. Scope of the quartz ceramics application is determined by complex of its unique properties [1, 2].

For example, the quartz ceramics is high-heat-resistant material with the low value of linear expansion coefficient (α = 300–1300 K = $(0.5–0.8)\cdot10^{-6}$ 1/K). It is characterized by excellent dielectric properties (ε = 2.7–3.6; tgδ = 0.0002–0.12) both at low and high temperatures, and by resistance to various corrosive media and other factors. At the same time, the quartz ceramics shows relatively low mechanical strength (σ_{flect} = 100–150 MPa, σ_{com} = 45–50 MPa) and only allows continuous operation at the temperatures not exceeding 1000°C [3].

The most common method of the quartz ceramics products manufacture is water slip casting in the porous plaster moulds followed by drying and burning at the temperatures of 1200– 300°C [4]. Advantage of this method is relative simplicity of the manufacturing process; principal disadvantage is low sedimentation stability of the slip, and hence instability of its rheological properties. In addition, production of close-packed products requires the burning temperature over 1200°C, at which quartz ceramics shows undesirable propensity to cristobalite crystallization resulting in considerable deterioration of the mechanical strength characteristics of the final product. These limitations can be eliminated by various ways.

Proposed methods of the slip rheology improvement are the following: grinding with multi-step loading of raw material [5, 6], introduction of granular filler [7], adjustment of the raw material to grinding media ratio in the disintegrating machine [8] and even introduction of various industrial wastes [9]. All these methods are intended mainly for production of the high-density slip with satisfactory indexes of fluidity and rate of wall build-up on the plaster mould surface. This means formation of the dense intermediate product as early as at the casting stage and facilitates production of the durable quartz material after burning. However, the burned ceramics is generally characterized by sufficiently high porosity within the range of 10–20 %, which does not allow production of the high-strength samples.

In order to reduce the ceramics porosity, researchers propose the use of additional product preparation operations: the intermediate product impregnation with the mixture of $Al(NO_3)_3$, tetraethoxysilane, ethanol and water [10] or silicone resin [11], the bulk product modification with silicone bonding adhesive after burning [12, 13], with methylphenylspirosiloxane followed by polymerization [14], with acetone solution of mixed silicone and phenolformaldehyde resins [15]. Such methods require additional resource and energy consumption, and may not always be implemented under industrial conditions.

In ceramics technology, the most reliable method of structural performance adjustment is the purposeful assurance of dense material sintering during the burning. Key problem of the quartz ceramics sintering is that sintering temperature and temperature of active cristobalite crystallization from the molten quartz fall in the same range. The formation of cristobalite, which changes in volume at the modification transformations [16], in the quartz ceramics during the burning results in the heat-resistance reduction, thermal expansion and product destruction (loosening). Due to the quartz ceramics cristobalitizing, it is challenge to produce the high-density products, and it is the reason of their low mechanical strength.

Thus, production of quartz ceramics with the minimum porosity values is an important and topical problem requiring to be solved taking into account the whole range of factors, namely: raw material availability at the selection of modifying additives, power consumption saving at the product heat treatment, maximum available technology for application under industrial conditions.

2. Experimental

One of the methods of slip rheological properties adjustment is introduction of the clay additives into slip composition. In this research, the dispersing agent — kaolin, of which chemical composition is resulted in Table 1, was introduced into the mixture composition for the purpose of improvement of the rheological-and-processing charac-

Table 1. Chemical composition of raw materials

Material	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	l.o.i.
Quartz tube scrap	99.70	0.12	0.02	0.01	0.05	0.05	0.03	0.02	0
Kaolin	45.14	38.27	0.31	0.50	0.67	0.4	0.8	0.25	13.66

Table 2. Rheological-and-processing characteristics of test slips

Mixture No.	Additive amount, wt. %	Suspension moisture content, %	No.0063 sieve residue, %	100 ml slip flow time, s	Sample drying shrinkage, %	5 mm wall build-up time, s
1	–	29.0	5.5	25	0.1	120
2	5	33.5	5.2	27	0.7	150
3	10	36.7	4.9	27	1.2	170
4	15	38.5	4.7	29	1.6	200

teristics of the quartz glass water suspension and the burned sample porosity reduction.

Subject of the research was production process of the quartz ceramics manufacture by the method of plaster-mould slip casting with the subsequent high-temperature burning [3].

Following tasks were set in this work: investigation and improvement of the slip rheological-and-processing properties for the purpose of ensuring its sedimentation stability and production of dense intermediate product easily removable from the plaster moulds; investigation of kaolin addition impact on formation of dense sintered material with the controlled phase composition and properties.

Quartz tube scrap was selected as basic raw material for the research.

After thorough cleaning of the raw material, experimental slips were prepared by the wet grinding of the quartz tube scrap in a porcelain mill. Suspension moisture content was controlled by gravimetric method and made 29–38.5 %, grinding readiness was determined by residue on the sieve No 0063. The slip was subjected by stabilization for 6 h at the continuous agitation. Test samples were made by plaster-mould casting method in form of plates of $3\times3\times0.5$ cm^3 in size with porosity of 42–45 %. An intermediate product was dried under the laboratory conditions, and then at the temperature of 100–120°C. The samples were burned in the laboratory oven with silicon carbide heater at the temperature of 1200°C for 18 h with heating of the samples for 7 h and holding at the maximum temperature for 2 h.

The following standard research methods were applied: ceramic slip moisture content determination from weight loss, grain size distribution determination by sieve method, slip rheological-and-processing properties determination with use of the Ford cup, drying shrinkage determination from the sample dimensions change, the burned sample water absorption capacity, porosity and density determination by hydrostatical weighing method, burned sample mechanical strength determination in a hydraulic press [17].

Amount of water added to suspension was determined from the flow time of 100 ml of the slip so that it was the same for all slips (within the range of 25±2 s.)

Burned sample phase composition was investigated by means of X-ray phase analysis [18] by DRON-3M machine with the use of X-ray tube with copper target cathode. Identification of crystalline phases was conducted with the use of X-ray photogram archive.

Test sample microstructure was investigated with the use of optical microscope MBS-10 in reflected light with magnification range from 8 to 56.

In this research, dispersing agent — kaolin was introduced into the mixture composition for the purpose of improvement of rheological-and-processing characteristics of quartz glass water suspension and burned sample porosity reduction. The additive was added to the slip made of the scrap quartz tubes; additive amount was 5, 10 and 15 wt. %. Suspensions were intimately mixed, and their moisture content was adjusted, since kaolin has a laminated structure, and its particles are prone to water absorption. Rheological-and-processing characteristics of the test slips are resulted in Table 2. In this work, the additive of kaolin, which is capable of to stabilize the slip even in the short-term rest state without agitation, was introduced in the quartz glass slip. Since kaolin has a package structure, it is capable of water absorption into the interpackage space and swells to various extent [19]. Hence, introduction of the kaolin additive and increase of its amount results in the increased amount of water required for the slip to achieve the pourable state.

3. Result and discussion

Data presented in Tables 1 and 2, show that with increase of the amount of kaolin being dispersing additive, achievement of the slip pourable state requires a greater amount of water, and suspension moisture

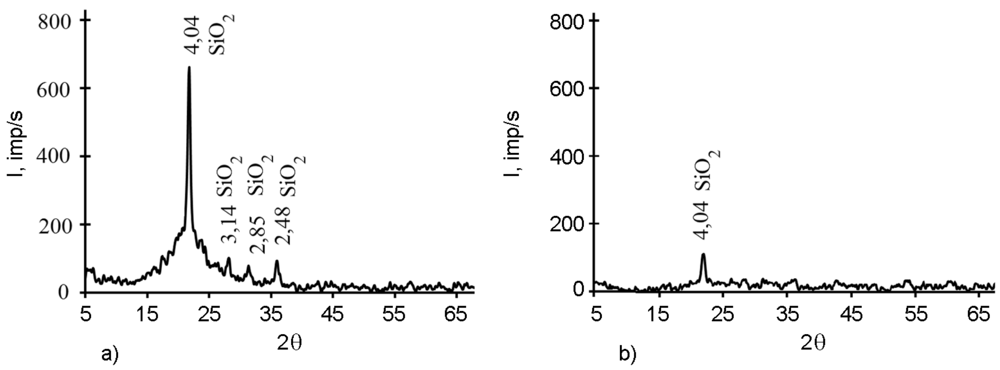

Fig. 1. X-ray photograms of quartz ceramics samples: a — without additive; b — with 10 wt. % of suspending additive.

content increases 1.4-fold at introduction of 15 % of the additive. Improvement of the rheological-and-processing characteristics, of which the major one is reduction of slip tendency to sedimentation, is observed for all slips. Suspension moisture content increase due to increase in amount of the dispersing additive results in the drying shrinkage occurrence and increase, which facilitates the intermediate product removal from the mould.

After burning, the samples showed the following properties (Table 3).

From the presented data it follows that the introduction of kaolin results in the considerable reduction of the burned sample water absorption capacity and open porosity. In addition, the compression strength is increased from 51 to 72 MPa.

The X-ray phase analysis shows (Fig. 1) that introduction of the additive results in the ceramic sample structure change. In the case of ceramics without additive, diffraction peaks typical for cristobalite (d = 4.04; 3.14; 2.85; 2.48 Å) are distinctly identified [20], while in the case of sample with 10 wt. % of kaolin, the principal peak of cristobalite is scarcely noticeable.

As can be seen from the obtained range of properties, introduction of kaolin as dispersing agent results in considerable change of the processing properties of the both slips and burned samples.

Rheological properties of the quartz glass-based slips are quite specific and cause a number of problems related to the product storage, transportation and casting. These are due to the hard fine quartz glass particles propensity to the rapid sedimentation, which considerably impairs processibility of such slip. The slip with a wide range of grain size distribution (from 5 to 63 μm and over), which in turn is required for formation of the close packing, segregates when in a quiescent state with coarser particles precipitating faster and finer ones precipitating slower. This causes formation of nonuniform-density casting, and results in development of internal stresses and enhances the further product susceptibility to cracking [21].

In addition, introduction of the additive affects also the slip fluid behavior and time of intermediate product wall build-up on the plaster mould surface. In spite of the fact that the build-up time increases from 120 to 200 s, the introduction of kaolin has beneficial effect on the physical and chemical processes of dewatering. Without the dispersing additive in the slip, water quite quickly diffuses in the plaster mould pores with dominance of vertical diffusion

Table 3. Physical-and-mechanical properties of test samples after burning

Mixture No.	Additive amount, wt.%	Water absorption capacity,%	Open porosity, %	Apparent density, g/cm^3	Mechanical compression strength, MPa
1	–	20.7	38.3	2.13	51
2	5	19.0	36.1	2.24	63
3	10	14.3	25.7	2.33	68
4	15	12.4	22.7	2.39	72

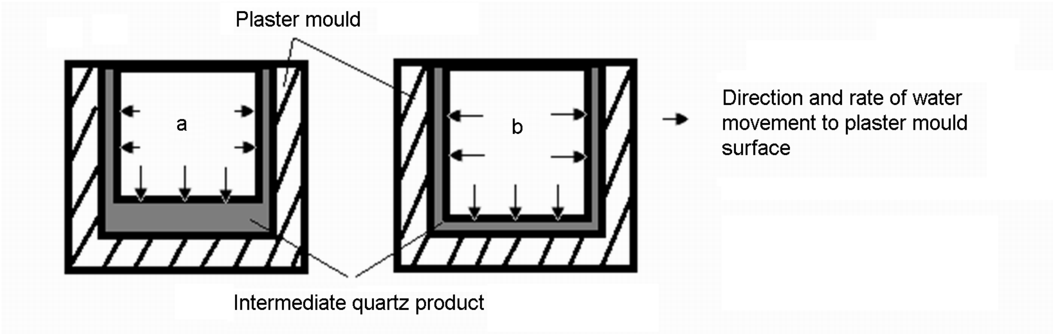

Fig. 2. Schematic diagram of intermediate product formation wall on the plaster mould surface: a — without dispersing additive; b — with dispersing additive in slip composition.

(Fig. 2a). And due to the difference in the dispersed particles size, these particles precipitate on the mould surface not so much due to the capillary forces, as due to the gravitation forces driving the solid phase sedimentation in the liquid phase. This results in the slip segregation and can result in formation of the nonuniform-density casting.

In the case of kaolin introduction, water removal becomes somewhat slower due to the high dispersion of the additive, however, dewatering occurs more uniformly (Fig. 2b) predominantly through the mould pores due to the capillary forces. In addition, the slip propensity to segregation in the quiescent state is considerably reduced, and hence distribution of the different grain size solid phase is more uniform and near the closest packing state [19]. In this case, determining factor is size of the dispersing additive particles (less than 3–5 μm), which fill interstices between the considerably coarser quartz glass particles produced by grinding (15–60 μm). Hence, the density is increased, as well as the dry intermediate product strength.

In addition, the kaolin introduction results in increased intermediate product drying shrinkage, which is not typical for the quartz glass-based slips [3]. However, ceramic mixture unshrinkability complicates its removal from the plaster mould after moulding. Surely, the minor shrinkage occurs due to the fact that drying removes hydration sheaths occurring around the quartz glass particles during the prolonged slip activation. Such activation requires continuous agitation of the quartz glass slip for about 3 days and over [3, 5]. In this case, introduction of the dispersing additive facilitates shrinkage processes in the quartz mixture; however, the intermediate product separation from the plaster mould walls is facilitated without application of such long-time activation.

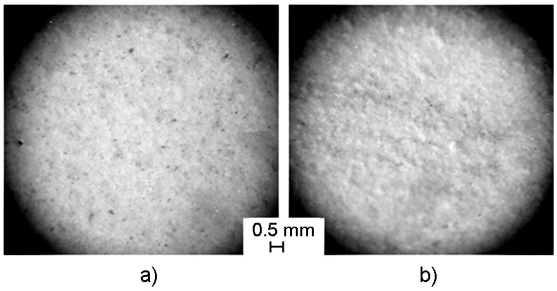

Fig. 3. Microstructure of samples: a — with 10 % wt. of kaolin additive; b — without additive, reflected light, magnification X48.

When sintering the quartz ceramics with the kaolin additive, a number of particularities is also observed. Firstly, due to formation of structure near to the closest grain packing (Fig. 3), the burned sample water absorption capacity is considerably reduced making 12.4 % in the case of samples with addition in amount of 15 wt. % as compared with 20.7 % in the case of the samples without additive.

In Fig. 3a showing sample with 10 wt. % of the tested additive in composition, one can see the virtually smooth surface where coarse quartz glass grains are uniformly distributed between the finer quartz glass and the dispersing additive grains. In contrast, the quartz ceramics sample without additive is characterized by rather loose structure with voids (pores) of about 0.1–0.3 mm. Such pores actively absorb water, which accounts for high water absorption capacity of the sample without additive (20.7 %).

Secondly, the tested additive introduction considerably reduces the material propensity to cristobalite crystallization during burning.

4. Conclusions

Thus, the conducted research shows efficiency of introduction of hydroalumosilicate as dispersing agent in the quartz ceramics manufactured by the plaster-mould casting. This considerably reduces slip propensity to sedimentation and improves uniformity of intermediate product wall build-up on the plaster mould surface. The intermediate product drying shrinkage is increased, which facilitates removal from the mould on the one hand, but on the other hand, this shrinkage should be taken into account at manufacture of the products with finish dimensions after shrinkage and burning. The additive introduction enhances the burned quartz material compression strength due to formation of the structure with more dense packing as compared with material without additive. This results in the burned material mechanical strength improvement and allows prediction of sufficiently high performance of the tested ceramics.

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