Дослідження стосуються фарфорових виробів, що отримують методом відливання у гіпсові форми з тонкодисперсних шлікерів. Було встановлено причини виникнення тріщин по краях виробів після утильного і политого випалу та запропоновано шляхи їх усунення.

В результаті комплексного дослідження базової керамічної маси заданого складу та виробів з неї було визначено ряд технологічних факторів, які обумовлюють розтріскування.

Визначення тонкості помелу виробничих шлікерів різних партій показало, що залишок на ситі № 0063 коливався від 0,7 до 3,5 %. Встановлений прямий взаємозв'язок між виникненням тріщин у виробах і підвищеним показником залишку, що сприяло розшаруванню керамічного шлікеру в процесі вистоювання в гіпсових формах. Зазначене призводило до виникнення внутрішніх напруг у структурі черепка. Іншим фактором, що обумовив розтріскування виробів, встановлено присутність у складі керамічної маси крупних зерен кварцу, які в процесі нагріву – охолодження здатні до модифікаційних перетворень. Окрім того, низька температура утильного випалу не сприяла завершенню процесів дегідратації глинистих та слюдистих мінералів, що посилювало внутрішні напруги у черепку.

Дослідження показали, що для забезпечення якісних показників керамічних виробів необхідно не тільки контролювати залишок на ситі, а й враховувати розподіл фракційного складу керамічного шлікеру, причому вміст кварцової складової розміром 30–63 мкм має становити не більше 12 мас. %. Зазначене сприяє утворенню щільного однорідного черепка з високим вмістом мулітової фази.

В результаті досліджень запропоновано також змістити температуру утильного випалу з 660 до 800 °С. Саме при цій температурі завершуються процеси дегідратації шаруватих силікатів та стабілізуються усадочні процеси.

Отримані результати можуть бути застосовані на типовому виробництві господарчо-побутових виробів із низькотемпературного фарфору

Ключові слова: шлікер, помел, кварц, водопоглинання, випал, фарфор, розтріскування, міцність, спікання, усадка

UDC 666.61
DOI: 10.15587/1729-4061.2020.204173

ANALYZING THE CAUSES OF CRACK FORMATION IN PORCELAIN AND THE WAYS TO ELIMINATE THEM

O. Khomenko
PhD, Associate Professor
Department of Ceramics and Glass
Ukrainian State University of Chemical Technology
Gagarina ave., 8, Dnipro, Ukraine, 49005
E-mail: elenahtks@ukr.net

B. Datsenko
PhD, Associate Professor, Senior Researcher
Department of Commodity Science and Commercial Activity in Construction
Kyiv National University of Civil Engineering and Architecture
Povitroflotskyi ave., 31, Kyiv, Ukraine, 03037
E-mail: bmd520@gmail.com

O. Hurzhii
PhD
Laboratory of Study of Materials, Substances and Products
Dnipropetrovsk Scientific Research Forensic Center
Budivelnyi dead end, 1, Dnipro, Ukraine, 49033
E-mail: gur2020ndekc@gmail.com

L. Savchenko
Senior Lecturer
Department of Architecture and Engineering Researches*
E-mail: sav.lida.76@gmail.com

O. Savchenko
PhD, Senior Lecturer
Department of Building Structures*
E-mail: savushka.sumy@gmail.com
*Sumy National Agrarian University
Herasyma Kondratieva str., 160, Sumy, Ukraine, 40021

Received date 03.04.2020
Accepted date 11.06.2020
Published date 30.06.2020

1. Introduction

Porcelain materials were used in manufacturing electrical insulating products, sanitary, and household ceramics, as well as ceramic granite [1, 2]. This is due to the high operational properties of this material – density, strength, durability, dielectric properties, which makes it possible to operate reliably the products for a long time [3]. However, porcelain has these characteristics only at ensuring proper technologies during its manufacturing.

The porcelain production is complex, multistage, and depends on many factors at each stage of the technological process [4–6], influencing the quality of the final product. In this connection, in case of occurrence of defects of products related to the disruption of production technology finding the causes and the ways of their prevention is quite complex and time-consuming.

Establishment of the patterns of the influence of technological factors of production on the quality of finished products is an important task for each enterprise, as it will make it possible to react promptly to these changes with a minimal negative impact on the products.

2. Literature review and problem statement

Porcelain is the subject of research for many scientists over the latest decades, but the improvement of the production technology of this material is still relevant. This is due to a variety of its types, compositions of ceramic masses and production methods, requirements for the quality of the finished product, and other factors. A wide range of scientific works [7–14] is devoted to the search for new raw materials and effective sintering additives.

Paper [7] deals with the influence of the colemanite additive on the intensity of porcelain sintering, paper [8] proposes introducing a wollastonite additive for the same purpose. However, papers [7, 8] do not consider any possible deviations from the technological process and their consequences.

Article [9] studies the possibility of using cullet and volatile ash as a fluxing component instead of feldspar in porcelain manufacture. Cullet was added in the amount of 10–25 % by weight and, it was found, based on determining the activation energy that the activity decreases at an increase of cullet. At the same time, article [10] indicates that the amount of cullet can be increased by up to 30 % by weight, and the firing temperature is reduced to 1,150 °C. The disadvantage of the cullet introduction to the porcelain composition is a tendency of a semi-finished product to deform during firing, which was not explored in these studies.

Paper [11] explored the possibility to replace quartz in the composition of the porcelain fired at the temperature of 1,200 °C. It was established that at the introduction of slag in the amount of 5–10 % by weight, the content of quartz residue in the structure of the fired material is really reduced, however, the mullite content decreases sharply from 20 to 2 % by weight. Instead, the anorthite crystalline phase is formed. Its effective influence on an increase in bending strength was found at the slag introduction in the amount of more than 20 % by weight. However, slag is a waste product of production and has an unstable chemical composition, which can cause deviations from the specified technological process, and this aspect was not considered in the study.

In article [12], the possibility of using nepheline-syenite as a fluxing component of the porcelain masses was established. The existence of nepheline-syenite in the amount of up to 15 % by weight contributes to a decrease in sintering time required to achieve low values of water absorption. In addition, the microstructure becomes more homogeneous, and mechanical characteristics increase. Similar ideas for expanding the raw material base of the fluxing components of porcelain and energy-saving aspects were outlined in paper [13]. However, papers [12, 13] contain insufficient information on what types of defects can occur when varying the compositions of ceramic masses and technological parameters.

In paper [14], the efficiency of the replacement of quartz sand with porcelain cullet in the production of high-voltage porcelain was found. Quartz was replaced with the cullet of products in the amount from 5 to 25 % by weight. It was determined that at the firing temperature of 1,250 °C, the mechanical compression strength of up to 89.7 MPa was achieved. The high strength of the samples is explained by an increase in the mullite phase in the structure of ceramic material, which is stimulated by introducing the cullet of porcelain products. The disadvantage of the research is that it does not consider the deformation processes, which can occur during firing due to the replacement of quartz with cullet.

Papers [15–18] contain the information about the studying of the peculiarities of the structure formation of a porcelain potsherd, the defects associated with modification transformations of quarts were examined. Article [15] deals with the occurrence of structural defects of porcelain at cooling from the temperature of 1,250 °C. Microcracks were found to occur at vitrification temperature (~800 °C) due to the mismatch of coefficients of thermal expansion of glass, mullite, and quartz particles. The process of occurrence of micro stresses flows at several stages and ends at a temperature of 300 °C. The radial cracking on quartz particles occurs between the vitrification temperature of 800 °C and the temperature of transition $\beta \rightarrow \alpha$. At the temperature of transition $\beta \rightarrow \alpha$, cracking is temporarily interrupted due to stress changes. At the temperatures below 500 °C, the cracks with less intensity appear around the particles, especially at a decrease in temperature below 300 °C, and there occurs the temperature of radial cracking of $\beta \rightarrow \alpha$ transition that appears on quartz particles. Studies [16] revealed the occurrence of microcracks around the quartz grain at the temperatures of 600–500 °C, which leads to a sharp drop in strength. However, specific recommendations concerning the way of preventing such defects are not given.

The influence of pyrophyllite additive on the peculiarities of porcelain structure formation was studied in paper [16]. Addition of 5–7.5 % of pyrophyllite as a substitute for clay improved the fire strength by about 24 % compared with the material without the additive, fired at 1,300 °C. Besides, amorphous SiO_2 freed from dehydroxylate pyrophyllite inhibits further recrystallization of mullite. The existence of a large quantity of undissolved quartz of a smaller size, as well as isolated pores in the microstructure of pyrophyllite-containing samples, prevents the spread of cracks and thus improves the mechanical properties. In paper [18], it is proposed to introduce pyrophyllite instead of quartz, which leads to the early occurrence of the liquid phase during firing and a decrease in thermal expansion of samples. The addition of up to 15 % of pyrophyllite led to a 29 % increase in strength. The above is related mainly with the elimination of stresses in the structure at a decrease in quartz content, as well as at an increase in the quantity of secondary mullite, distributed all over the volume of material. However, we must bear in mind that the pyrophyllite, unlike quartz, is much more actively dissolved in the melt, that is a large amount of glass is formed, as well as large elongated pores, distributed in the matrix, which leads to worsening of mechanical properties. Quartz sand in a ceramic mass contributes to decreasing shrinkage and deformation during firing [17]. In papers [17–19], there are not enough practical recommendations for the technological parameters of the process. In addition, these studies do not reveal the influence of other components of the ceramic mass on the possibility of occurrence of micro stresses in porcelain, which causes such type of defect as cracking.

However, as studies [20, 21] showed, the formation of the microstructure of ceramics and its properties depend on the complex of technological factors of production, so it is necessary to consider the reasons for the occurrence of a particular type of defect in a complex.

Thus, numerous scientific studies in the field of porcelain improvement are aimed at the expansion of the raw material base, improvement of operational properties of products, and a decrease in power consumption of production, but there is very little information about the analysis of possible causes of defects of products. That is why when the problems of faulty products or a decrease in quality arise under production conditions, the search for the ways of their elimination requires a comprehensive approach.

Therefore, it is advisable to conduct comprehensive research into manufacturing porcelain products within one technological process – from the choice of raw materials to the formation of the structure of the final product. It is thus possible to trace the causes of occurrence of a particular defect and to find ways of its elimination.

3. The aim and objectives of the study

The aim of this study was to establish the technological parameters of the production process, which will ensure the formation of a dense structure of products without defects after firing.

To achieve the aim, the following tasks were set:

– to research the rheological and technological properties of the ceramic mass and the products from it, which have a defect of "edge cracking";

– to study the dependence of the porcelain properties on the fineness of grinding of the ceramic mass;

– to determine the temperature of the bisque firing of a ceramic potsherd.

4. Materials and methods to study the production of fine ceramic masses and experimental samples

For the research, we selected the ceramic mass and the technology of manufacturing low-temperature porcelain under production conditions, in which the products' defect of "edge cracking" occurred. The slip composition of the basic ceramic mass is the following, % by weight: refractory clay – 12.5; concentrated kaolin – 21.5; quartz sand – 17.3; alkaline kaolin – 45.3; cullet of products – 3.4. Above 100 % by weight of dry matter, ceramic slip included electrolytes, % by weight: soda – 0.32; liquid glass – 0.06. The temperature of bisque firing was 660 °C and that of glazed firing –1,250 °C.

The rheological properties of the slips and physical-ceramic characteristics of the samples were assessed by the standard methods. The fineness of grinding was determined by the indicator of residue on sieve No. 0063. The indicator of the slip fluidity, which represents the time of flowing of 100 ml of suspension through the hole of 4 mm, was measured with the help of the Ford dish. Plasticity number was determined by the difference in the moisture content of the mass at its transition from the plastic state into the fluidity state and from the plastic state into the dry state. Shrinkage indicators were determined by a change in the dimensions of the samples – semi-finished products before and after drying and firing. Water absorption of sintered materials was assessed by the amount of absorbed water in open pores of a sample after the saturation in a vacuum and with the help of hydrostatic weighing.

The character of thermal transformations of ceramic masses was determined with the help of differential-thermal analysis using the derivatograph of the system of F. Paulik, J. Paulik, L. Erdey Q – 1000 (the "IOM" company, Hungary) at the heating rate of 5 °C/min.

Qualitative mineralogical composition of the residue on a sieve No. 0063 was determined by the petrographic method with the help of the optical microscope MBS-10 (PA "Rubin", Russia).

The fractional composition of the experimental slips was determined with the help of the sedimentograph "FRITSCH" (Germany) "Analysette microtec".

X-ray phase analysis was performed with the help of X-ray analyzer DRON–3 ("Burevisnyk", Russia) with Cu radiation.

To study the microstructure of the fired samples, the raster electronic microscope "REM-106 – I" (SPC "Akademprylad", Russia) was used.

5. Results of studying porcelain with a "cracking edge" defect

5. 1. Studying the rheological and technological properties of slips and fired products

Production of porcelain, due to the existence of numerous technological operations, is quite complicated and the search for the cause of occurrence of any defect should consider "foreseeing" it at any stage. That is why the cracks on products' edges that occurred after bisque or glazed firing (Fig. 1) not systematically from batch to batch, could be caused by the factors of each previous stage (grinding, molding, drying). Consequently, the comprehensive studies of the industrial slip and the products fired from it were conducted to identify the reasons for a defect.

a *b* *c*

Fig. 1. Edge defects of products from ceramic mass: *a* – on the bend of a product; *b* – on the handle, c – on a flat area

Rheological properties of factory slips of the uniform composition, selected during different shifts, are given in Table 1.

Table 1

Rheological properties of factory slips

No. of sample	Moisture content of slip, %	Fluidity of slip, s	Residue of sieve No. 0063, %	Existence of cracks in fired products
1	33.2	17	2.3	++
2	34.5	21	0.7	–
3	34.1	20	0.8	+
4	32.9	16	3.5	+++
5	33.6	16	3.1	++
6	33.9	20	1.2	+

Our studies showed that fluctuations in the indicators of moisture content and fluidity of the slips of different batches were insignificant. Most attention was attracted by the indicators of residue on sieve No. 0063, which changes from 0.7 % to 3.5 % at the values recommended for porcelain – up to 0.5 % [19].

The stratification capability of slips was determined by the indicators of residue on sieve No. 0063 in the samples selected at the top and the bottom part of the tank having a height of 20 cm. Samples were taken during slip settling for 1.5 hours, which is the average indicator of time taking the wall of a semi-finished product on the surface of the gypsum mold. The results are shown in Fig. 2.

At the lengthy rest, the samples of slips in varying degrees are actually capable of stratification. Thus, for sample No. 1 after 1.5 hours of settling, the residue on sieve No. 0063 at the upper part of the tank is 0.7 %, and in the lower part, this indicator reaches 2.4 %, since most of the stone particles settle on the bottom of the vessel. In slips No. 2 and No. 3, the residue on sieve No. 0063 is lower (0.7–0.8 %), and thus the stratification is smaller – the difference between the residue on sieve No. 0063 in the upper and in the lower parts of the tank is insignificant.

During the study of the mineralogical composition of the residue on sieve No. 0063, it was found that its prevailing amount is represented by quartz grains (Fig. 3) and only in a small amount – by feldspar and mica minerals.

Fluctuations in the fineness of the mass lead to a change in its drying and firing properties (Table 2).

Overall, the basic ceramic mass refers to low-plastic (plasticity number is less than 7). On the one hand, such masses rather quickly take the wall on the surface of a gypsum mold during product casting, but on the other hand, such masses are more prone to stratification in a resting state. In addition, low-plastic masses have a low binding capacity, which makes them prone to cracking during drying or firing. Table 2 shows that masses No. 1, 4–6, for which the elevated indicator of residue on sieve No. 0063 was established, have lower plasticity indicators in comparison with masses No. 2, 3.

Shrinkage and water absorption indicators correlate with the fineness of slips: the more the residue on a sieve, the lower the shrinkage indicators and the less dense the structure of the potsherd is formed during sintering.

During the analysis of data on the technological process, attention was paid to a rather low temperature of the bisque firing of ceramic products – 660 °C. Differential thermal analysis was performed in order to establish the behavior of the ceramic mass at heating. The results for sample No. 6 are shown in Fig. 4.

The resulting data suggest that at the temperature of the bisque firing of 660 °C, the process of dehydration of laminated clay minerals are incomplete and the formation of a potsherd that is relatively stable in terms of shrinkage extends up to 800 °C.

Table 2

Properties of ceramic mass after drying and firing

No. of sample	Plasticity number*	Air shrinkage, %	Fire shrinkage after firing at 660 °C, %	Water absorption after firing, at 660 °C, %
1	3.6	2.7	8.2	19.0
2	4.4	3.7	9.0	18.1
3	4.5	3.7	9.1	18.2
4	3.2	2.5	7.8	21.5
5	3.2	2.5	7.8	21.5
6	4.1	3.1	8.6	19.2

*Note: * – to determine plasticity number, plastic masses were obtained from slips using the drying method*

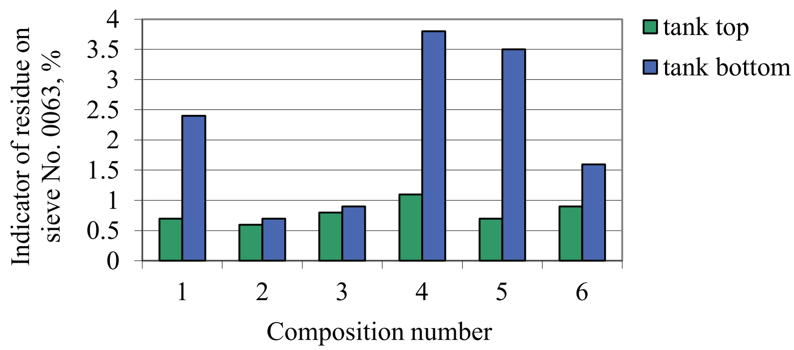

Fig. 2. Determining the stratification capacity of slips

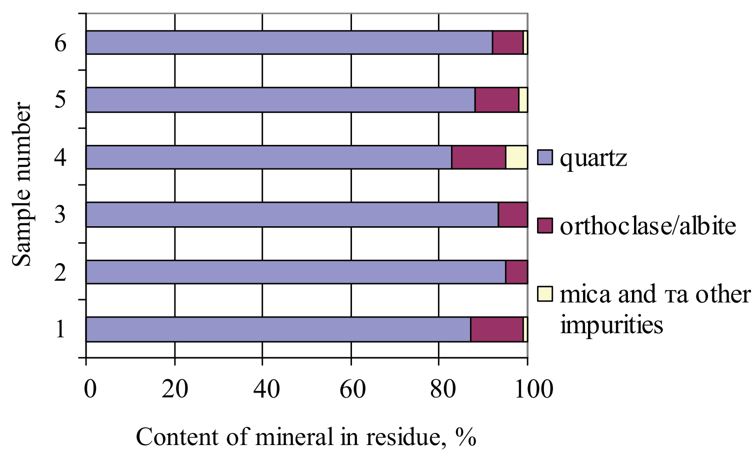

Fig. 3. Mineralogical composition of residues on sieve No. 0063 of experimental samples

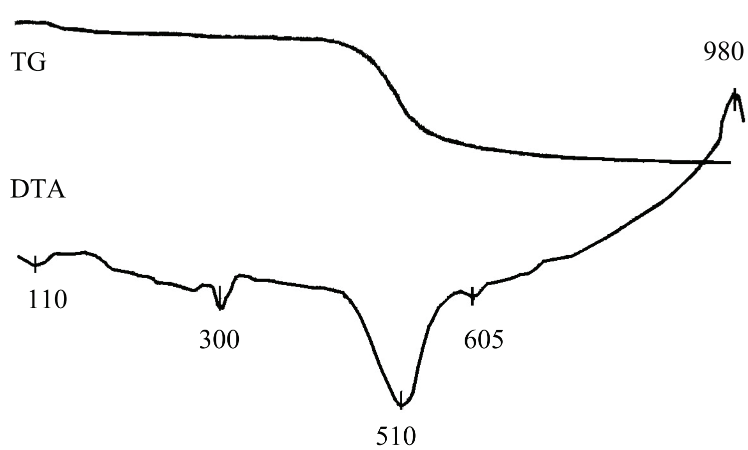

Fig. 4. Results of differential-thermal analysis of sample No. 6

5. 2. Studying the dependence of product properties on the fineness of grinding a ceramic mass

Data from Table 1 show that for samples No. 2 and 3 with the same residue on sieve No. 0063, cracks in products of a batch are found during grinding (0.7–0.8 %) in one case, while in the other case – they are not. It was assumed that the estimation of the fineness of the ceramic mass according to the indicator of the residue on a sieve is insufficient. Quartz grains of the dimensions of less than 63 μm (passing through the mentioned sieve) can be also subject to modification transformations with volume changes. Thus, they can also cause cracks as larger grains. Then it was decided to study how the duration of grinding can affect a change in the distribution of the granulometric composition of slip particles, including quartz.

Grinding for ceramic slip sample No. 6 was continued under laboratory conditions. Ceramic slip in the amount of 500 g was loaded into a porcelain drum with the ratio of slip: grinding bodies, which is close to factory-related (1:1.4), and sampling for studying the grinding capacity of components was made every 20 minutes. The data in Fig. 5 show that at almost the same residue on sieve No. 0063 of 0.5–0.7 % (samples 2–5), the distribution of fineness of the particles of a slip by fractions is different.

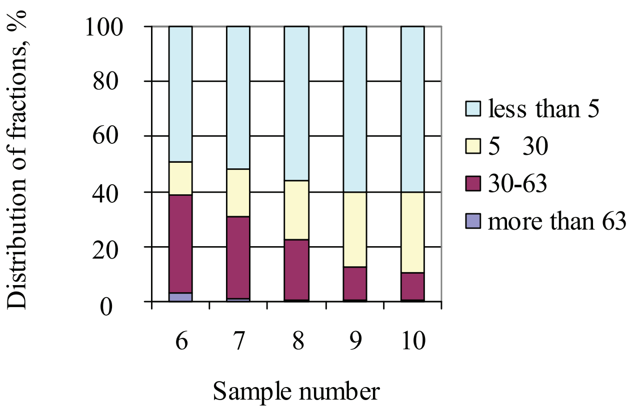

Fig. 5. A change in the ratio of slip fractions during grinding

Thus, samples No. 7 and No. 8 both have the residue on sieve No. 0063 of less than 0.7 %. However, the content of a medium fraction of dimensions of 30–63 μm, which is represented mainly by quartz grains in these slips, is different: it is 31 % for sample No. 7, and 22 % for sample number 8.

In this case, the structure of porcelain after firing becomes denser and more homogeneous (Fig. 6).

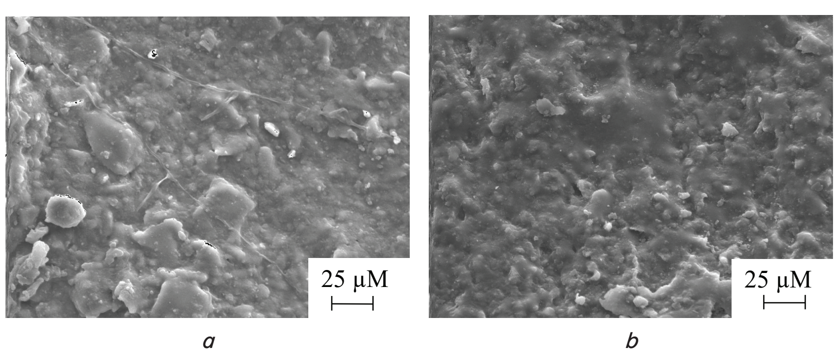

Fig. 6. Microstructure of experimental slips after firing the samples at 1,250 °C: *a* – No. 7, *b* – No. 9

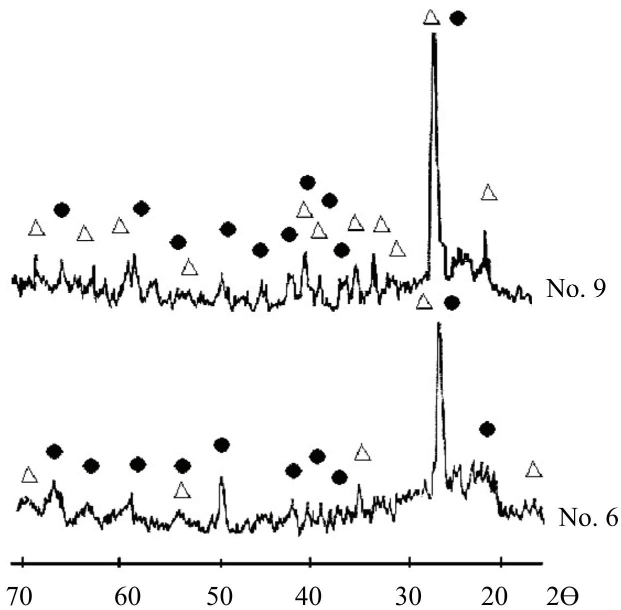

Fig. 7. Radiograms of experimental samples: Δ – mullite, • – β – quartz

Change in fineness of the ceramic mass also influences the phase composition of the fired potsherd. Radiograms of samples No. 7 and No. 9 are shown in Fig. 7.

Sample No. 9, which is made from a slip of finer grinding, contains a reduced amount of quartz (the diffraction maxima of quartz have lower intensity). Instead, the amount of the mullite phase due to the greater homogeneity of the mass and more complete flow of the sintering process is higher.

5. 3. Choosing the temperature of the bisque firing of ceramic mass

The bisque firing of a ceramic semi-finished product is intended to form a ceramic potsherd before applying the glazed layer. In this case, strength should be sufficient to perform the glazing operation, and the high porosity of a bisque potsherd should ensure the adhesion of a coating with the ceramic base before gazed firing. However, as shown by differential-thermal research into the ceramic masses (Fig. 5), the bisque firing temperature of 660 °C is insufficient in terms of completeness of the process of dehydration of clay minerals.

Therefore, the degree of sintering of ceramic mass was studied in the subsequent study in the interval of 660–850 °C. Ceramic samples from slip No. 9 were fired in a laboratory furnace within the specified temperature range with the pitch of 40 °C, and sintering degree was determined by the indicator of water absorption and shrinkage (Fig. 8).

Fig. 8 shows that the shrinkage process extends to the temperature of 800 °C, and then comes a period, in which the indicators of shrinkage and water absorption of the experimental samples remain constant. That is, we can assume that the process of dehydration of clay minerals and mica existing in the ceramic mass completes exactly at the indicated temperature.

Given the results obtained, it is appropriate to increase the temperature of bisque firing from 660 to 800 °C.

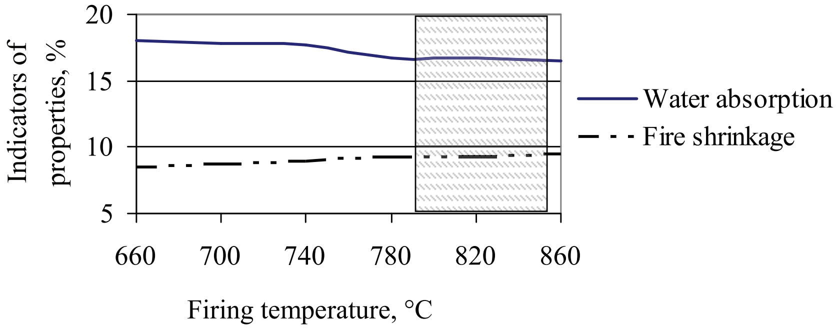

Fig. 8. Determining the sintering of ceramic samples of composition No. 9

products showed the dependence of the intensity of defect occurrence: the higher the indicator of residue, the greater the slip stratification and the larger the number of products having cracking.

The study of the mineralogical composition of the residue on a sieve made it possible to establish that 82 % of it is represented by quartz grains. The existence of coarse-grained quartz in the composition of the porcelain mass can also cause cracking of ceramic products due to modification transformations when heating, and especially, when cooling the products [15, 16]. That is why, given an increased content of quartz in residues, it could be argued that their existence could also provoke cracking in the experimental samples.

The paper also explored the conditions for grinding ceramic slips (Fig. 5) and their impact on the granulometric composition of the porcelain mass. It turned out that the residue indicator is insufficient to assess the suitability of a slip of the assigned composition to manufacture high-quality porcelain products. The estimation of the ratio of the fractions in the slip is not of less importance, because the quartz of the dimensions of 30–63 μm also poses a danger in terms of internal stress in the structure of a potsherd during the firing-cooling.

The difference in the content of the medium fraction can explain why cracks were found in on a batch of products and were not found in another batch at the same residue on a sieve (Table 1).

At the prolonged time of grinding, the ratio of the fractions is changed, but there is a moment when the energy consumed for grinding virtually does not affect the crushing of grains under these conditions. The example of samples No. 9 and No. 10 can show that they have almost the same distribution of fractions, so it does not make sense to continue grinding. However, when you compare samples No. 7 and No. 9, the content of a fraction of 30–63 μm decreases almost threefold from 35 % to 12 %. This means that the overwhelming number of quartz grains acquires the dimensions of less than 30 μm, which is optimal in terms of preventing negative consequences of modification transformations [21].

Fig. 6 shows the microstructure of the samples, made from samples No. 7 and No. 9. In both samples, a sufficient amount of vitreous phase is formed during firing to provide liquid-phase sintering and formation of a dense potsherd. However, in the presence of quartz with the prevailing dimensions of 30–63 μm in the mass, the structure is less homogeneous – in the break of the potsherd, there are clearly pronounced non-dissolved quartz grains immersed in the basic vitreous mass. In the presence of the quartz grains of the dimensions of 5–30 μm, the fired sample has a more homogeneous structure, without any large unchanged fragments of quartz.

The differential-thermal analysis (Fig. 4) showed the existence of four endo effects on the DTA curve. The endo effect with the maximum at 110 °C is associated with the removal of physically bound water from the kaolinite component of the ceramic mass. At the same time, small mass losses were recorded on the TG curve. The endo effect with the maximum at 300 °C is associated with the partial decomposition and the destruction of the structure of hydro-mica and the burnout of organic impurities contained in the ceramic

6. Discussion of results of improving the technological process aimed to reduce defects

Using the example of a particular production, the properties of ceramic slip and fired products were studied in order to identify the causes of the occurrence of cracks on the edges after bisque and glazed firing.

The study of the rheological properties of factory slips made it possible to detect systematic disturbances of the grinding mode from batch to batch towards an increase in the residue on sieve No. 0063, which changed from 0.7 to 3.5 % (Table 1). The increased content of coarse fraction in the porcelain mass cannot only help to speed up the rate of taking a wall on the surface of the gypsum mold but also increase the stratification capacity of a slip in a free state. If this is the case, non-uniform casting can manifest itself in the form of deformation and cracking at the subsequent stages.

To prove this hypothesis, the stratification capacity of slips was determined (Fig. 2). It was found that the samples of slips with increased residue on sieve No. 0063 had a strong stratification tendency in the process of settling. In the state of rest, large stone particles quickly settled down onto the bottom of the tank, and only fine clay particles remained in the upper part [22].

Having simulated this difference during casting into a gypsum mold, it is possible to see that a change in the slip fineness causes a difference in shrinkage processes in the upper-lower part of the product (Fig. 9). The difference in shrinkage causes deformation and causes internal stresses in a semi-finished product, which may be uncontrollably manifested during subsequent thermal treatment of the product.

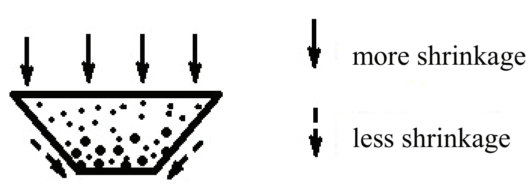

Fig. 9. Distribution of shrinkage deformation at a violation of the slip grinding mode

Samples No. 2, 3 appeared to be most stable among the experimental samples. For these samples, there was a minimum discrepancy between the indicator of the residue on sieve No. 0063, selected from the upper and lower parts of the tank in the state of long rest. If we have a look at Table 1, we will notice that for products made from these slips, the minimum edge cracking was recorded.

Thus, the ratio of fineness of grinding and the stratification capability of slips with the existence of defects of mass. The endo effect of high intensity with a maximum of 510 °C is associated with dehydration of the kaolinite mineral, that is, the removal of chemically bound water from the structure of clay mineral kaolinite and mica. The effect is of high intensity because kaolinite is introduced both by clay, and kaolin, and alkaline kaolin, that is, its content in the mass is up to 45 % (because according to the calculations by the TG curve, the mass losses are 6.7 %). And, finally, the endo effect at 605 °C is associated with the final destruction of the mica components of the slip. By the intensity of the endo effect, it can be argued that there is not less than 5–8 % of mica in the sample of the ceramic mass since it is not a high-intensity effect, but still, it is recorded on the DTA curve. The final weight loss associated with dehydration, judging by the TG curve, finishes at 780–800 °C.

The exo effect with a maximum of 980 °C is associated with the crystallization in the structure of the primary mullite material with kaolinite.

Thus, as the final dehydration of silicates ended at higher temperatures than the temperature of the bisque firing of products, the shrinkage processes in the mass were not completed, which could lead to cracking of products at the second firing as well. This is completely in line with the constructed concept of the occurrence of cracks in the items of this production. Given the results of the sintering of the ceramic mass (Fig. 8), it would be advisable to increase the temperature of bisque firing from 660 to 800 °C.

Thus, the conducted research revealed the factors that caused the appearance of cracks in the fired products. Recommendations for the production were given, and the changes in the product quality were tested after the production. The results of the improvement of the technological process are given in Table 3.

Thus, the results of the research into the basic ceramic mass revealed the instability of the grinding of ceramic slip, which led to its stratification and provoked the occurrence of internal stresses in the structure of products and led to their cracking at various stages of firing. The second factor which contributed to the occurrence of cracks was the existence of coarse quartz grains, which undergo modification changes during heating-cooling. It was established that the additional factor that caused cracks, even at the glazed firing, was the too low temperature of bisque firing, at which the process of dehydration of clay materials did not have enough time to be completed and intensified the emergence of internal stresses during the second firing.

As a result of the implementation of research results in the production, it was possible to eliminate the edge cracking.

However, it should be noted that reaching the recommended indicators of the technological process at every particular production depends significantly on the nature of raw materials and the slip composition of the ceramic mass, features of the design of grinding, molding and firing equipment, the quality of coolant and the environment in the furnace and other conditions. That is why the development of production technology with a minimum number of defects requires an individual approach.

These studies are appropriate to direct at further research into the relationship of "defect – structure – technological parameters", covering as many deviations from the normal flow of the technological process of production of porcelain that provoke the emergence of various types of defects. Such studies will facilitate the improvement of production quality.

Table 3

Results of improvement of the technological process

Indicator	Before the study	After the study	Notes
Stability of grinding conditions by the residue of sieve No. 0063	0.7–3.5	0.5–0.7	Careful control over the slip fineness at the beginning of the technological process made it possible to enhance the product quality
Maximum indicators of residue on sieve No. 0063, %	3.5	0.7	An increase in the fineness of grinding of the ceramic mass resulted in a decrease in slip stratification in the process of casting and a decrease in the difference in shrinkage processes on the product height
Content of the fraction of 30–63 µm in ceramic liqueur, %	Not measured	Up to 12	Control of the content of this faction in the slip made it possible to decrease the amount of "residual quartz" in porcelain with the tendency of modification transformations
Temperature of bisque firing, °C	660	800	An increase in the temperature of the bisque firing of the semi-finished product made it possible to obtain a more stable formed structure of a potsherd
Existence of cracks on the edge	Found in 14 % of the products	no	The complex of proposed measures for adjusting of grinding and firing modes made it possible to eliminate cracks in products

7. Conclusions

1. The research into the rheological and technological properties of the ceramic mass and products from it revealed that the defect of "edge cracking" is caused by a complex of factors. These factors include instability of the grinding conditions of the ceramic slip, insufficient fineness of grinding of the mass components, and low temperature of the bisque firing of a semi-finished product. Due to the difference in shrinkage in various parts of the product, there occurred internal stresses in the structure of a ceramic potsherd, which was manifested in the appearance of cracks.

2. The studies of the dependence of the porcelain properties on the fineness of grinding of the ceramic mass revealed that the content of the fraction of 63–30 µm in the amount to 12 % in the slip is rational in order to obtain high quality produce. This makes it possible to decrease the content in porcelain of "residual quartz", capable of modification transformations.

3. To prevent the occurrence of the cracking defect of porcelain products, it was recommended to increase the temperature of bisque firing up to 800 °C.

Thus, to prevent the occurrence of a cracking defect, it is recommended to implement the complex of the following measures: to ensure the constancy of the indicator of residue on sieve No. 0063 of not more than 0.5–0.7 %; to develop the grinding mode so that the slip should not contain more than 12 % of the fraction of 63–30 µm; to increase the temperature of bisque firing up to 800 °C.

References

1. De Miranda, S., Patruno, L., Ricci, M., Saponelli, R., Ubertini, F. (2015). Ceramic sanitary wares: Prediction of the deformed shape after the production process. Journal of Materials Processing Technology, 215, 309–319. doi: https://doi.org/10.1016/j.jmatprotec.2014.07.025
2. Dal Bó, M., Medina, F. (2018). Chemical tempering applied to Spanish porcelain tiles. Boletín de La Sociedad Española de Cerámica y Vidrio, 57 (5), 207–212. doi: https://doi.org/10.1016/j.bsecv.2018.03.002
3. Bernasconi, A., Diella, V., Pagani, A., Pavese, A., Francescon, F., Young, K. et. al. (2011). The role of firing temperature, firing time and quartz grain size on phase-formation, thermal dilatation and water absorption in sanitary-ware vitreous bodies. Journal of the European Ceramic Society, 31 (8), 1353–1360. doi: https://doi.org/10.1016/j.jeurceramsoc.2011.02.006
4. Marinoni, N., Diella, V., Confalonieri, G., Pavese, A., Francescon, F. (2017). Soda-lime-silica-glass/quartz particle size and firing time: Their combined effect on sanitary-ware ceramic reactions and macroscopic properties. Ceramics International, 43 (14), 10895–10904. doi: https://doi.org/10.1016/j.ceramint.2017.05.126
5. Tunçel, D. Y., Özel, E. (2012). Evaluation of pyroplastic deformation in sanitaryware porcelain bodies. Ceramics International, 38 (2), 1399–1407. doi: https://doi.org/10.1016/j.ceramint.2011.09.019
6. Kivitz, E., Palm, B., Heinrich, J. G., Blumm, J., Kolb, G. (2009). Reduction of the porcelain firing temperature by preparation of the raw materials. Journal of the European Ceramic Society, 29 (13), 2691–2696. doi: https://doi.org/10.1016/j.jeurceramsoc.2009.03.029
7. Akpinar, S., Evcin, A., Ozdemir, Y. (2017). Effect of calcined colemanite additions on properties of hard porcelain body. Ceramics International, 43 (11), 8364–8371. doi: https://doi.org/10.1016/j.ceramint.2017.03.178
8. Turkmen, O., Kucuk, A., Akpinar, S. (2015). Effect of wollastonite addition on sintering of hard porcelain. Ceramics International, 41 (4), 5505–5512. doi: https://doi.org/10.1016/j.ceramint.2014.12.126
9. Yürüyen, S., Toplan, H. Ö. (2009). The sintering kinetics of porcelain bodies made from waste glass and fly ash. Ceramics International, 35 (6), 2427–2433. doi: https://doi.org/10.1016/j.ceramint.2009.02.005
10. Njindam, O. R., Njoya, D., Mache, J. R., Mouafon, M., Messan, A., Njopwouo, D. (2018). Effect of glass powder on the technological properties and microstructure of clay mixture for porcelain stoneware tiles manufacture. Construction and Building Materials, 170, 512–519. doi: https://doi.org/10.1016/j.conbuildmat.2018.03.069
11. Dana, K., Das, S. K. (2004). Partial substitution of feldspar by B.F. slag in triaxial porcelain: Phase and microstructural evolution. Journal of the European Ceramic Society, 24 (15-16), 3833–3839. doi: https://doi.org/10.1016/j.jeurceramsoc.2004.02.004
12. Esposito, L., Salem, A., Tucci, A., Gualtieri, A., Jazayeri, S. H. (2005). The use of nepheline-syenite in a body mix for porcelain stoneware tiles. Ceramics International, 31 (2), 233–240. doi: https://doi.org/10.1016/j.ceramint.2004.05.006
13. Ryshchenko, M. I., Fedorenko, E. Y., Chirkina, M. A., Karyakina, É. L., Zozulya, S. A. (2009). Microstructure and properties of lower-temperature porcelain. Glass and Ceramics, 66 (11-12), 393–396. doi: https://doi.org/10.1007/s10717-010-9209-4
14. Rodríguez, E. A., Niño, C. J., Contreras, J. E., Vázquez-Rodríguez, F. J., López-Perales, J. F., Aguilar-Martínez, J. A. et. al. (2019). Influence of incorporation of fired porcelain scrap as partial replacement of quartz on properties of an electrical porcelain. Journal of Cleaner Production, 233, 501–509. doi: https://doi.org/10.1016/j.jclepro.2019.05.403
15. Chmelík, F., Trník, A., Štubňa, I., Pešička, J. (2011). Creation of microcracks in porcelain during firing. Journal of the European Ceramic Society, 31 (13), 2205–2209. doi: https://doi.org/10.1016/j.jeurceramsoc.2011.05.045
16. Štubňa, I., Trník, A., Vozár, L. (2007). Thermomechanical analysis of quartz porcelain in temperature cycles. Ceramics International, 33 (7), 1287–1291. doi: https://doi.org/10.1016/j.ceramint.2006.04.024
17. Mukhopadhyay, T. K., Ghatak, S., Maiti, H. S. (2009). Effect of pyrophyllite on the mullitization in triaxial porcelain system. Ceramics International, 35 (4), 1493–1500. doi: https://doi.org/10.1016/j.ceramint.2008.08.002
18. Mukhopadhyay, T. K., Ghosh, S., Ghatak, S., Maiti, H. S. (2006). Effect of pyrophyllite on vitrification and on physical properties of triaxial porcelain. Ceramics International, 32 (8), 871–876. doi: https://doi.org/10.1016/j.ceramint.2005.07.002
19. Khomenko, O. S. (2018). Choice of ceramic masses for the manufacture of electrical ceramics. Voprosy Khimii i Khimicheskoi Tekhnologii, 1, 92–95. Available at: http://nbuv.gov.ua/UJRN/Vchem_2018_1_15
20. Khomenko, E. S., Purdik, A. V. (2017). Particulars of Microstructure Formation in Clinker Ceramic. Glass and Ceramics, 74 (1-2), 48–51. doi: https://doi.org/10.1007/s10717-017-9926-z
21. Stathis, G., Ekonomakou, A., Stournaras, C. J., Ftikos, C. (2004). Effect of firing conditions, filler grain size and quartz content on bending strength and physical properties of sanitaryware porcelain. Journal of the European Ceramic Society, 24 (8), 2357–2366. doi: https://doi.org/10.1016/j.jeurceramsoc.2003.07.003
22. Khomenko, E. S. (2017). Impact of kaolin addition on properties of quartz ceramics. Functional Materials, 24 (4), 593–598. doi: https://doi.org/10.15407/fm24.04.593