Rheological properties of a slip based on synthesized slavsonite and properties of ceramic materials based on it

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Abstract

The effect of thinning additives on the rheological properties of an aqueous slip based on the crystalline phase of slavsonite ($SrAl_2Si_2O_8$) has been studied. The influence of the properties of the slips under study on the performance characteristics of the created ceramics was established. The positive effect of the Dolapix PC 67 thinning additive in an amount of 0.1 wt. % has been shown. A decrease in the moisture content of the slip from 40% to 30%, and an improvement in the performance parameters of the developed ceramic materials is achieved.

Keywords: slavsonite, dense-sintered ceramics, slip, rheology, thixotropy,
Kulcsszavak: szlavszonit, sűrűn szinterezett kerámiák, öntő massza, reológia, tixotrópia

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1. Introduction

The direction of research, part of which is described in this article, is the synthesis of the necessary crystalline phases with low dielectric properties and the technology of manufacturing products of complex geometric shape on their basis. In previous studies, a technology for the solid-phase synthesis of the required crystalline phase, namely slavsonite ($SrAl_2Si_2O_8$), at a reduced temperature was created [1,2]. The next stage is to establish the optimal technological conditions for casting products from an aqueous slip, which will make it possible to obtain dense sintering of a ceramic radio-transparent material.

In the study [3], it was found that heavy Sr^{2+} ions with close packing in the crystal lattice of anorthite weakly react to heating from room temperature to 1000°C and above in ultrahigh frequencies of electromagnetic radiation. Their insufficient participation in thermal ionic relaxation is expressed in low values of dielectric losses, therefore slavsonite is characterized by the following properties: dielectric constant $\varepsilon \leq 6...8$, tangent of dielectric loss angle $tg\delta \leq (1...50)\cdot10^{-4}$, low TLEC $\leq 3.8\cdot10^{-6}$ K^{-1}; and also has a high melting point of 1654°C and high mechanical strength (E = 110...115 GPa) [4].

The relevance of the direction and study as a whole is to ensure a combination of low dielectric properties and high mechanical properties of slavsonite when obtaining a dense-sintered ceramic radio-transparent material by slip casting.

2. Analysis of literature data and problem statement

Today there are various options for forming ceramic products, but the most popular is casting. This method is based on the properties of materials to absorb and release water. Slip casting into porous molds is an individual method of formation, associated primarily with the different nature of the physicochemical interaction of materials with the liquid medium chosen for casting. For each material, it is necessary to select a liquid phase, the dispersion of the solid phase and methods of its grinding, stabilization conditions, stabilizers, and their ratio. Despite the peculiarities of slip casting into porous forms of many materials, the general technological scheme for manufacturing products using this method remains constant and consists of the following:

- making molds and preparing them for casting;
- preparation of the dispersed phase and dispersion medium;
- preparation of slip;
- casting;
- removal of the casting;
- drying of castings;
- firing or sintering.

In the production of many types of technical ceramics, the introduction of the clay component into the slip is not allowed. The dispersed phases of clayless slips generally differ from clay minerals in a lower dispersion, lower adsorption capacity, and hydrophilicity.

The main characteristics of slips are viscosity and the associated fluidity. Slip viscosity determines their ability to fill forms. All other things being equal, it can be adjusted by the ratio of the solid and liquid components in the slip, and it is also adjusted using thinning additives.

The effectiveness of stabilization and thinning of such slips is primarily determined by the value of the generated potential. The most common method for thinning such suspensions is to adjust their pH.

In suspensions of oxide materials that do not contain clay, structure formation is associated mainly with the partial dissolution of the solid phase. The properties of such suspensions are controlled by changing the pH of the medium and the introduction of surfactants [5]. Oxide particles, unlike clay particles, can form both negative and positive micelles. So, the minimum viscosity of the oxide suspension can be achieved by adding both acidic and alkaline electrolytes in a certain amount or by bringing the suspension to a certain pH value. For oxide suspensions, usually the lowest viscosity is obtained at pH = 2.5-4 with the addition of acid or pH = 10-12.5 with the addition of alkali. However, the introduction of alkali metal ions into oxide aqueous suspensions (slips) is almost always undesirable or even unacceptable, since their presence can reduce some properties of finished products, mainly electrophysical [6].

To give the necessary mechanical strength to cast and dried products, it is recommended to introduce up to 5% organic additives into the suspension [6]. The authors of [7] proposed a method for obtaining high-density aqueous slips with the addition of HCl or NH_4Cl as a stabilizer in the amount of 1.0-2.0 ml per 1 liter of slip, which leads to a decrease in the time of blank formation and a decrease in rejects when producing large-sized products.

The authors of the study [8] found that the introduction of complex SBFF (phloroglucinol furfural modifier) + STPP and SBFF + TPPN + NaOH additives into a ceramic slip promotes an increase in the density of finished products by 5-10% compared to samples containing additives C-3 + TPPN and reotan + TPPN. An increase in the mobility of a slip with the proposed complex additives indicates an increase in its aggregate resistance, which leads to a more uniform distribution of particles of the dispersed phase. This, in turn, contributes to the uniform distribution and reduction of the pore size in the sample, and affects the thermal conductivity coefficient.

Thus, it is advisable to study the properties of aqueous slips, adjusting them by the above methods, and to establish their effect on the characteristics of finished products.

3. The purpose and objectives of the study

The aim of the study was to establish the optimal technological conditions for casting slavsonite products from water slips, which would make it possible to obtain dense sintering of ceramic radio-transparent material.

To achieve the goal, the following tasks were set:

- to study the nature of fluidity and the level of thixotropy of slips;
- to study the influence of inorganic and organic thinning additives on rheological and technological properties (both under the condition of the individual action of thinning additives and with their complex use);
- to optimize slip properties (fluidity, thickening), which determine the quality of molding products by casting into porous forms;
- to produce prototypes, study their performance properties, which determine the quality of finished products.

4. Rationale for the choice of thinning additives for research

Dolapix PC 67 has a wide deflocculation range and counteracts thixotropy. Since the product is liquid and thus completely dissociates into ions, the deflocculating effect begins immediately after addition. This process is the result, on the one hand, of the cationic exchange of the additive with the slip, as well as the influence on this double electric layer of mineral particles. On the other hand, polymer chains attach to mineral particles and thus affect steric repulsion [9].

Stellmittel ZS prevents sedimentation, the optimal addition ranges from 0.05 to 0.3% dry weight, depending on individual working conditions. The most suitable way to add Stellmittel ZS is to thoroughly mix it in a slip shortly before casting the samples into molds [10].

Sodium tripolyphosphate (STPP) is the most common deflocculant in the polyphosphate class and has significant fluidizing properties. Polyphosphate anions are well adsorbed by slip particles, significantly increasing their negative charge. As a result, the viscosity of the ceramic suspension decreases [8]. The thikening effect occurs very quickly when very small amounts of solution are added. It is recommended to inject it into the slip in an amount of not more than 0.1% on dry matter – this is half or one teaspoon of the solution per 1 liter of slip. Tripolyphosphate is introduced into foundry masses only if absolutely necessary; it is better to use water glass or soda ash. A slip containing tripolyphosphate can be very liquid, but at the same time it slowly builds up the shard, and the product tends to “stick” to the wall of the mold [11].

5. Materials and methods

At the preliminary stage of research [12], the optimal composition of the masses was established and low-temperature synthesis of slavsonite was carried out; all subsequent studies were carried out using this synthesized powder. Slip preparation took place in a ball mill. Rheological properties (fluidity and thickening) were studied depending on the moisture content of the slip without additives and with thinning additives.

Depending on the type of ceramic, the rheological properties of the slip will have slightly different values, so the fluidity and thickening factor for porcelain slip – 10-15 s and 1.8-2.2 for semi-porcelain slip – 15-20 s and 1.9-23 s, and for faience – 15-25 s and 1.5-2.6 s [6]. The average runoff time for normally prepared slips is: for porcelain masses – 10 s, semi-porcelain masses – 15 s and earthenware masses – 20 s, and the thickening coefficient for high-quality slips used in fine ceramics is in the range of 1.8-2.2 [13]. For slips based on alumina, the optimal fluidity is within 4-10 s [14]. In view of the absence of these indicators for slavsonite ceramics, in the conditions of the pouring method, it was decided to focus on the average values – fluidity 15 - 25 s, thickening coefficient 1.7 – 2.5. The fluidity and thickening of the slips were determined using an Engler viscometer.

To reduce the fire shrinking of the samples, it is necessary to maximize the density of the slip while maintaining its rheological properties; therefore, the task was set to obtain a slip with better properties at a moisture content of 25 - 30%.

The samples were fired in a laboratory muffle furnace Nabertherm HTCT 01/16 at a temperature of 1350°C with a holding time of 2 hours.

The main characteristic, on the basis of which the degree of sintering can be estimated, is water absorption, and an important characteristic that makes it possible to evaluate the closed porosity is the apparent density. These characteristics, as well as open porosity, were investigated by the "express vacuumation" method according to ISO 5017:2014.

6. Research results

The results of determining the rheological properties of the slip are presented in *Table 1*.

Additive	Slip moisture, %	Slip fluidity, s	Slip thickening
No additive	40	7	-
	35	14	-
	30	-	-
Dolapix PC 67 (0.1 wt.%)	30	19	1.75
	28	22	1.67
	26	28	1.65
Stellmittel ZS (0.1 wt.%)	30	25	2.1
	28	27	1.84
	26	35	-
Sodium tripolyphosphate (0.1 wt.%)	30	20	1.73
	28	22	1.65
	26	30	1.61

Table 1 Rheological properties of the slip
1. táblázat Az öntő massza reológiai tulajdonságai

The performance properties of the samples were also determined, the slip was poured into pre-dried gypsum molds, and the appearance of the gypsum molds is shown in *Fig. 1*. In the absence of clay components in the slip and, accordingly, practically zero air shrinkage, at this stage, filter paper was laid in the gypsum molds. This made it possible to freely remove the workpiece from the mold after the set of the shard. There was also a low mechanical strength of the workpieces, which manifested itself in the form of chips under slight pressure. The fired ceramic samples were characterized by the absence of defects, and had significant porosity and low density.

Fig. 1 Plaster mold during casting
1. ábra Gipsz öntés során

From the data obtained, it can be seen that the slip without additive and at a moisture of 40% and 35% is characterized by high fluidity, and at a moisture of 30% the slip is too thick. According to the change in the properties of the slip, with the addition of the Dolapix PC 67 thinning additive, its positive effect is observed, the fluidity of the slip at a moisture of 30% is 19 s, the fluidity at a moisture of 28 and 26% is satisfactory, but the thickening coefficient is lower than the required values – 1.66 and 1.65, respectively, which indicates a narrow range of casting properties and, accordingly, the thixotropy of the slip. As for the expediency of using the Stellmittel ZS additive, it can be concluded from the experiment that this additive is better used as a slip stabilizer. Sodium tripolyphosphate, as a thinning additive, has less effect on the rheology of the slip (fluidity – 20 s, thickening capacity – 1.73). Since, under the same conditions, the slip with Dolapix PC 67 additive has better flow and thickening values, it is more expedient to use this additive.

After heat treatment, the performance properties of the samples were determined using industry-specific methods. The results of studies of the properties of samples cast from a slip with optimal properties are presented in *Table 2*.

Additive	Slip moisture, %	Firing shrinkage, %	Water absorption,%	Open porosity, %	Relative density, g/cm³
No additive	40	24.8	11.6	23.0	2.03
	35	16.1	10.5	21.6	2.01
Dolapix PC 67 (0.1 wt.%)	30	12.5	10.2	21.5	2.11
	28	11.8	9.7	21.2	2.18
	26	11.2	8.8	19.6	2.23

Table 2 Properties of samples cast from a slip with optimal characteristics
2. táblázat Az optimális jellemzőkkel rendelkező öntvények tulajdonságai

For clarity, on the basis of the data obtained, a graphic interpretation of the properties of the obtained ceramic samples depending on the water content in the slip and the thinning additive was built (*Fig. 2*).

The data obtained indicate that a decrease in the moisture content of the slip from 30 to 26% improves the properties with a linear dependence. Water absorption and open porosity decrease from 10.2% to 8.8% and from 21.5% to 19.6%, respectively, and the apparent density increases from 2.11 to 2.23 g/cm³.

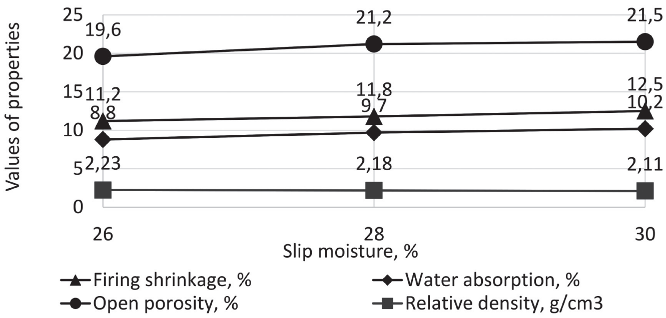

Fig. 2 Properties of the obtained samples of slavsonite ceramics after firing at a temperature of 1350°C depending on the moisture of the slip with the addition of Dolapix PC 67 thinner

2. ábra A szlavszonit kerámiaminták tulajdonságai 1350 °C hőmérsékleten történő égetés után, az öntő massza nedvességétől függően, Dolapix PC 67 hígító hozzáadásával

7. Discussion of the results

In this study, the main part of attention was directed to the development of technological parameters for obtaining an aqueous slip based on slavsonite with optimal rheological properties. The purpose of this decision was to establish the optimal technological conditions for casting products by studying the change in the moisture content of the slip and the use of thinning additives.

The choice of moisture content and the introduction of thinning additives made it possible to solve two problems. The first one is to achieve the required rheological properties of the slip while reducing the moisture content from 35% to 30%. The second one is to improve the properties of fired ceramic specimens: to reduce water absorption and increase the apparent density by 10%.

As a result of the experimental studies, it was possible to improve the rheological properties of the slip with a decrease in moisture, but it should be noted that indicators of water absorption and open porosity, as well as low values of the apparent density of the created ceramic samples have high values. This indicates a low density of the cast blank, and also negatively affects the mechanical characteristics of the cast products. Therefore, in subsequent studies on the rheology of the slip, it is planned to additionally conduct an experiment to determine the rate of gain and the strength of the shard. To reduce thixotropy, it is planned to additionally use stabilizing additives, and conduct casting on the vibrating table.

8. Conclusions

It has been experimentally established that a slip based on a slavsonite crystalline phase, even at a moisture of 40%, is characterized by a high level of thixotropy.

The influence of inorganic and organic thinning additives, namely Dolapix PC 67, Stellmittel ZS and sodium tripolyphosphate, has been investigated. Based on rheological and technological studies, it was established that Dolapix PC 67 in an amount of 0.1 wt. % imparts optimum properties to a slip with a moisture content of 30% (fluidity – 19 s, thickening – 1.75).

The resulting ceramic prototypes are characterized by the following parameters: water absorption – 10.2%, apparent density – 2.11 g/cm^3, fire shrinkage – 12.5%.

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