UDC 666.5

MICROSTRUCTURE AND PROPERTIES OF LOWER-TEMPERATURE PORCELAIN

M. I. Ryshchenko,[1] E. Yu. Fedorenko, [1,2] M. A. Chirkina,[1] É. L. Karyakina,[1] and S. A. Zozulya[1]

Translated from *Steklo i Keramika*, No. 11, pp. 26 – 29, November, 2009.

The technological properties of a series of granite rocks are studied, and it is shown that they can be effectively used as fluxes for porcelain mixes. It is found that low-temperature porcelain can be obtained under intensified heat-treatment. The phase composition, microstructure, and properties of the materials are studied. The effect of the properties of the liquid phase on the formation of structure and the usage and decorative properties of porcelain fabricated by energy-conserving technology are determined.

Key words: lower-temperature porcelain, flux, granites, mullite formation, liquid phase, energy-conserving technology.

Today, the once flourishing porcelain industry in Ukraine is going through difficult times. The production of porcelain dishware is down sharply, and the number of manufacturers has decreased. This situation is largely due to the high cost of gas as the main energy carrier used by ceramic enterprises, the dependence on imports of quartz feldspar raw materials, and inadequate modernization of the industry's technological stock [1].

One promising solution to this problem is to decrease the heat-treatment temperature of porcelain articles while maintaining high aesthetic-use properties and quality. Wide adoption of the low-temperature porcelain technology will give more than a few advantages to domestic manufacturers. The main advantages are lower energy usage and shortening of the technological cycle. This makes the development of new mix compositions for fabricating porcelain articles for household use by means of accelerated low-temperature firing very topical.

[1] National Technical University "Kharkov Polytechnic Institute," Kharkov, Ukraine.
[2] E-mail: fedorenko e@ukr.net.

It is known that fluxes — natural materials classified type 1 and 2 fluxes which promote the formation of melt during firing — are usually added to mixes to intensify the sintering of ceramics. Feldspars, pegmatites, leucocratic granites, petalitic rock, nepheline-syenites, and perlites are widely used as fluxes. The use of industrial wastes obtained from the production of low-iron granite rock as a fluxing component in ceramic mixes is economically justified for the production of porcelain articles for household use.

The objective of the present work is to obtain low-temperature porcelain with water absorption $\leq 0.5\%$ and to study the relationship between its properties and structure. Granite siftings obtained during the development of the Anadol'skoe, Kremenevskoe, and Andreevskoe granite deposits (Donetsk Oblast') were used as fluxes in the porcelain mixes with lower-temperature firing; the chemical composition of these granites is presented in Table 1.

The fluxing capacity of the granite rocks chosen for the present investigations was determined using an express method, based on the physical – chemical analysis of rock-forming systems, to determine the composition and proper-

TABLE 1.

Granite deposit	Content, wt.%								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	others
Andreevskoe	70.70	15.70	1.69	0.14	1.60	1.01	4.70	3.86	0.60
Anadol'skoe	71.97	15.97	0.87	0.07	0.81	0.12	3.73	4.48	1.89
Kremenevskoe	70.44	17.35	0.67	0.05	1.62	0.31	4.54	3.70	1.41

TABLE 2.

Melt characteristic	Temperature, °C	Granite deposit		
		Andreevskoe	Anadol'skoe	Kremenevskoe
Amount, %	1150	94.56	93.68	98.20
	1200	97.44	95.11	98.65
	1250	100.00	95.88	99.10
Viscosity (log η), Pa · sec	1150	3.84	3.78	3.67
	1200	3.48	3.46	3.58
	1250	3.40	3.34	3.26
Surface tension, N/m	1150	0.283	0.281	0.287
	1200	0.286	0.289	0.284
	1250	0.289	0.286	0.291
Activity, arb. units	1150	0.091	0.106	0.121
	1200	0.097	0.105	0.122
	1250	0.079	0.104	0.120

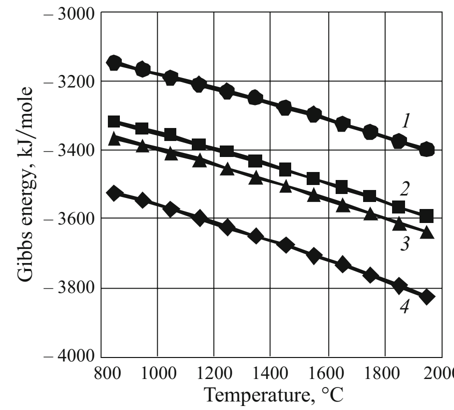

Fig. 1. Temperature dependence of the Gibbs energy of the mullite formation reactions in the porcelain mixes developed (wt.%): *1*) 50 Anadol'skoe granite sifting; *2*) 50 Kremenevskoe granite sifting; *3*) 55 Anadol'skoe granite sifting; *4*) 55 Kremenevskoe granite sifting.

ties of melts formed during heat-treatment of the materials [2]. The viscosity and the surface tension of the rock melts for the temperature interval 1150 – 1250°C were calculated taking account of the additive character of these properties by means of I. A. Makhovskaya's method [3]. The activity of the melts was evaluated by the method proposed by G. Zal'mang [4]. Analysis of the computed properties of the rock melts formed by melting of the granites studied (Table 2) suggests that the rocks with the most effective fluxing action come from the Andreevskoe and Anadol'skoe deposits. These rocks are capable of forming in the temperature interval 1150 – 1250°C melt in amounts 95 – 97% with relatively low viscosity ($10^{3.46}$ – $10^{3.48}$ Pa · sec) and surface tension within the norms (0.25 – 0.30 N/m) [5].

Kremenevskoe granite forms at 1200°C a larger amount of melt (98.65%) with higher viscosity (log η = 3.58), but compared with Andreevskoe granite it contains less iron oxide, which is a big advantage for obtaining articles with higher whiteness.

A visual examination of the products of firing of the rocks at 1200°C showed that Andreevskoe granite melt has a greenish-grey color, which indicates the presence of darkly colored minerals in the rock. For this reason, granite siftings produced during the development of the Anadol'skoe and Kremenevskoe deposits, were used as the fluxing components in the subsequent development of the porcelain mixes.

The lower-temperature porcelain mixes developed contain the materials: clayey components (white-burning refractory clay from the Dryzhkovskoe deposit and dry-enrichment kaolin from the Glokhovetskoe deposit) and fluxing components (Kremenevskoe and Anadol'skoe granite siftings). The amount of clayey components varied in the range 38 – 43% and the amount of sinter intensifiers was 50 – 55%. A melt modifier (dolomite) in the amount 3% and 5% alumina as an additional source of Al_2O_3, required to form mullite with the participation of excess quartz obtained from the decomposition of kaolinite, were also added to the mixes.

To determine the probability of mullite formation during the formation of lower-temperature porcelain a thermodynamic analysis was performed of this reaction from Al_2O_3 and SiO_2, whose amount corresponds to the molar content in the composition of the porcelain mixes (N_i and M_i):

$$N_i\,Al_2O_3 + M_i\,SiO_2 \rightarrow 3Al_2O_3 \cdot 2SiO_2.$$

The computational results are presented in Fig. 1.

Analysis of the data showed that mullite is likely to form during the heat-treatment of all experimental mixes. The calculation of the phase composition of the products of firing of the mixes developed (Table 3) established that the maximum

TABLE 3.

Flux content in the experimental mix, wt.%		Mullite content, wt.%	Glass phase content, wt.%				Free quartz content, wt.%
Kremenevskoe granite sifting	Anadol'skoe granite sifting		Na_2O	K_2O	Al_2O_3	SiO_2	
50	0	20.03	2.61	2.55	7.06	24.91	31.43
55	0	20.72	2.40	2.44	6.60	23.29	30.62
0	50	13.30	2.20	3.03	6.91	24.39	34.26
0	55	14.59	2.07	2.86	6.45	22.99	34.73