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Investigations on Properties of Sintered Ceramics out of Low-Melting Illite Clay and Additive of Fine-Dispersed Nepheline Syenite

Jolanta PRANCKEVIČIENĖ*, Valdas BALKEVIČIUS, Alfonsas Algimantas ŠPOKAUSKAS

VGTU Scientific Institute of Thermal Insulation, Linkmenų 28, LT-08217 Vilnius, Lithuania

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The work deals with the ceramics obtained by burning of formative mixtures out of low-melting illite clay with additives of mineral wool centrifugation waste (MWCF waste) and fine-dispersed nepheline syenite. For investigations, we used milled nepheline syenite with specific surface of 8200 cm^2/g. After burning of formative mixture with 25 % additive of milled nepheline syenite at temperature of 1060 ºC, the sintered ceramics with water absorption of 2.52 % and density of 2097 kg/m^3 was received. The temperature of local liquid phase origination was observed at 800 ºC. The ions K^+ and Na^+ contained in nepheline syenite reacted with the compounds contained in clay and, at crystallization of reaction products, leucite and aegirine formed.

Keywords: mineral wool centrifugation waste, low-melting illite clay, nepheline syenite, leucite, aegirine.

INTRODUCTION

Low-melting clays are suitable for production of sintered ceramics only after correction of their chemical and granulometric composition [1]. As a leaning additive for production of sintered ceramics, usually quartz sand is employed. The properties of such ceramics and behaviors of sintering process are investigated sufficiently well [2, 3]. Various additives can be admixed to clays to correct sintering characteristics of formative mixtures, and among these additives, of importance are fluxing and fibre mineral materials [4 – 13].

The literature provides data on numerous researches on properties of sintered ceramic materials obtained upon burning of formative mixtures made out of clay and a leaning additive, such as sand. During sintering of a similar silicate system, the origination of liquid phase is influenced by various additives. These additives may be divided into two groups. One group consists of additives containing earth alkaline metal oxides, while the other containing alkaline metal oxides [14]. It was revealed that additives of the first group admixed to formative mixtures decrease the temperature for liquid phase origination by 50 ºC – 80 ºC. From the X-ray diffraction analysis one can see that MgO containing additives, when admixed to clay, cause crystallization of spinel and cordierite. In case of additives containing CaO, one gets helenite, anorthite and wollastonite crystallized. The authors underline that due to alkaline metal oxides-containing additives admixed to kaolinatic clays, the temperature of liquid phase origination drops by 80 ºC – 120 ºC [14].

To reveal the impact of additives containing earth alkaline metal oxides on properties of sintered ceramic body, the investigations were carried out [7 – 10]. The glass systems SiO_2-CaO-MgO-Na_2O and SiO_2-Ba_2O_5-Na_2O were investigated to learn the impact on clay containing 50 % kaolin. It was found out that the addition of 30 % waste of such glass results in sintered ceramics with compressive strength increased by 30 % – 40 % and sintering temperature decreased down to 1100 ºC [10]. A possibility to employ fluxing additives (waste glass) in the production of porcelain articles was investigated as well [7 – 9]. From the results of investigations made, one can maintain that added 10 % waste glass forces the sintering temperature to decrease and the values of strength characteristics to increase [9]. The sources of literature indicate that for correction of clay sintering characteristics, the additive of nepheline syenite is useful. Upon comprehensive dilatometric investigations of formative mixtures composed of kaolinatic clay and nepheline syenite additive [6], it was discovered that after addition of 10 % nepheline syenite into clay, the viscosity of liquid phase, which originates during the process of sintering, decreases. The author Sedmale investigated the peculiarities of formative mixtures composed of hydromicaceous clays, sand and nepheline syenite, as a fluxing additive [15]. It appeared that after addition of 15 % nepheline syenite to hydromicaceous clay, within range of temperatures from 1060 ºC to 1150 ºC, the received sintered ceramics had water absorption of ≤ 2 % and density of (1.91 – 2.4) g/cm^3. The data of literature show that in the production of sintered ceramic articles another leaning component may be used, i. e. mineral wool centrifugation waste (MWCF waste) [16, 17]. This waste is a silicate system SiO_2-Al_2O_3-CaO-MgO, which is obtained during stringing of mineral wool melt [17]. It was discovered that if to admix 20 % MWCF waste to low-melting clay one can receive sintered ceramics [16]. However, no information exists about the impact of fluxing additives on sintering characteristics of such ceramics and on properties of sintered ceramic body. Therefore, wider investigations are indispensable for clearing up these issues.

This investigation was launched to find the sintering behavior of formative mixtures composed of clay, leaning additive – MWCF waste and fluxing additive of nepheline syenite and the properties of received sintered ceramics.

TEST METHODS

The chemical composition of raw materials used for the investigation is provided in Table 1.

*Corresponding author. Tel.: +370-5-752381; fax: +370-5-2752629.
E-mail address: *eglaina@gmail.com* (J. Pranckevičienė)

Table 1. Chemical composition of the raw materials

Raw materials	Chemical composition, %							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	R_2O	TiO_2	l.o.i.
Clay	46.67	17.93	6.70	8.90	4.26	3.22		12.25
MWCF waste	42.13	18.30	5.81	16.15	13.94	1.73	2.02	1.40
Nepheline syenite	44.80	28.60	2.60	1.20	0.60	19.50		0.90

Clay was dried to constant mass at temperature of 105 ºC ±5 ºC in the not ventilated dryer. Dried clay was milled in a vertical stone mill and sieved through a sieve with mesh of 1.0 mm. Mineral wool centrifugation waste was roasted at temperature of 500 ºC and sieved through the sieve with mesh of 2.0 mm.

Nepheline syenite was dried at temperature of 105 ºC ±5 ºC to constant mass in not ventilated dryer. Afterwards nepheline syenite was milled in the ball mill by dry method.

For investigations, three series of formative mixtures were prepared. The compositions of formative mixtures are presented in Table 2. To the formative mixtures T1 and T2, milled nepheline syenite was added. For comparative investigations, the formative mixture T3 was prepared with addition of not milled nepheline syenite.

Table 2. Compositions of the formative mixtures

Formative mixture	Clay	MWCF waste	Nepheline sienyte	Milled nepheline syenite
T1	70	20		10
T2	55	20		25
T3	65	20	15	

The molded samples (50×50×50 mm) were dried under natural laboratory conditions. Next the samples were dried to constant mass at temperature 105 ºC ±5 ºC.

For evaluation of deformation of samples, the special stamps were made. After measuring of distances between stamps in dried and burnt samples, the drying shrinkage (S_{dr}) and burning shrinkage (S_b) were calculated according to the following formulae:

$$S_{dr} = \frac{l_0 - l_1}{l_0} \cdot 100 \quad \%, \tag{1}$$

$$S_b = \frac{l_1 - l_2}{l_1} \cdot 100 \quad \%, \tag{2}$$

where l_0 is distance between stamps in not dried sample in mm; l_1 is distance between stamps in dried sample in mm; l_2 is distance between stamps in burnt sample in mm.

The prepared samples were burnt at temperatures of 950, 1000, 1040, 1060, 1080 and 1100 ºC. The burnt and dried samples were subjected to weighing and measuring of their height, width and length.

The ultrasonic testing of dried and burnt samples was performed by apparatus PUNDIT-7, the water absorption was determined according to the standard LST EN 771-1.

The X-ray diffraction analysis of burnt samples was carried out by X-ray diffractometer DRON-7 (copper anode, anode tension 30 kV, current 12 mA, radiation CuK_α), phase composition was identified basing on ASTM file of reference data.

The thermographic investigations were conducted by derivatograph LINSEIS STA PT-1600, air being environment of investigation and at temperature rise speed of 10 ºC/min.

The dilatometric investigations were made by dilatometer LINSEIS L76 at temperature rise speed of 5 ºC/min. The samples were heated up to temperature of 1070 ºC, air being environment of investigation. The granulometric composition and specific surface of milled nepheline syenite were determined by apparatus FRITCH ANALYSETTE 22.

RESULTS AND DISCUSSION

In the technology of products of sintered ceramics, besides the leaning component (sand), the fluxing additives are used to reduce the viscosity of the liquid phase, which is forming during the sintering. Using such additives, it is possible to correct the processes running in the course of generation of sintered ceramic body, as well as the properties of the latter [11 – 13]. In recent years the researches were performed to the aim of finding out of possibilities to use nepheline syenite in aluminosilicate systems. L. Esposito *et. al.* investigated the effect of nepheline syenite additive containing 15.4 % oxydes of alkaline metals ($Na_2O + K_2O$) on properties of sintered ceramic material [18]. The formative mixtures were prepared out of high-melting kaolin clays and the leaning component, sand. The samples were burnt at maximal temperature of 1260 ºC. A. Salem *et. al.* performed the dilatometric measurements of such formative mixtures and analyzed the effect of nepheline syenite additive on consistent patterns of shrinking in high-melting kaolin clays [6].

When using low-melting illite clays for preparation of formative mixtures, the maximal temperature of burning of samples is considerably lower [4, 15]. The study dealt with the ceramic material received upon burning of samples out of low-melting illite clay, leaning component (MWCF waste) and fluxing additive, nepheline syenite containing 19.5 % oxydes of alkaline metals ($Na_2O + K_2O$) (Table 1). The maximal temperature of burning of samples is 1100 ºC.

For formative mixtures T1 and T2, milled nepheline syenite was used with the specific surface of 8200 cm^2/g. The average diameter of particles of milled material was 9.79 μm. The size distribution of particles of milled nepheline syenite is provided in Fig. 1. For comparative investigations, the formative mixture with added 15 % not milled nepheline syenite was prepared (average diameter of particles was 198.02 μm).

The drying and burning shrinkages of molded samples were measured. The average value of drying shrinkage for the samples T3 was 7.2 % (Table 1). After addition of

milled nepheline syenite into formative mass and after increasing of percentage of this additive from 15 to 25 %, the value of drying shrinkage decreased down to 5.7 %.

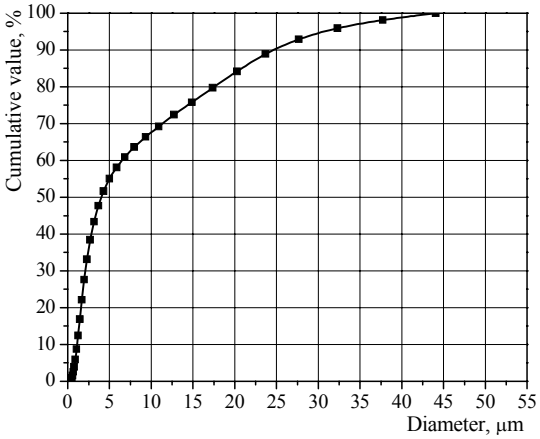

Fig. 1. Distribution of particles of milled nepheline syenite by size

Table 2. Drying shrinkage of molded samples

Formative mixture	Drying shrinkage, %
T1	5.7
T2	5.9
T3	7.2

Analyzing the data of burning shrinkage, one can state that the samples of series T1 and T3 shrink evenly during burning (within temperature interval of 950 ºC to 1060 ºC) and the values of burning shrinkage within this interval practically do not differ (Fig. 2). The values of burning shrinkage for the samples of series T1 burnt at 1060 ºC made 3.5 % and those of series T3 – 4.0 %. The comparative analysis of investigation data showed that increase of the percentage of milled nepheline syenite in formative mixture from 10 % to 25 % (Sample T2), brings to the values of burning shrinkage within 950 ºC – 1060 ºC that are higher than those of samples T3 and T1 (Fig. 2). It was established that the maximal value of burning shrinkage for the sample T2 was 6.0 %, achieved upon burning of samples at temperature of 1060 ºC.

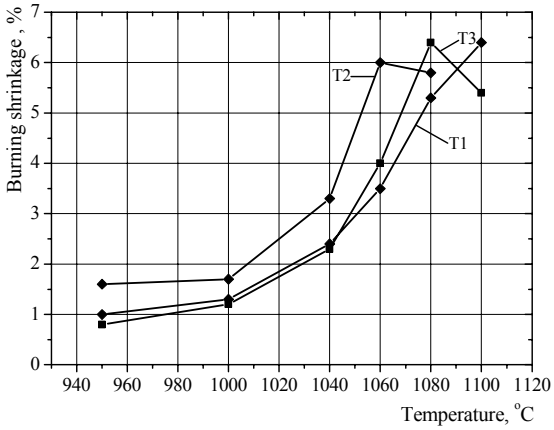

Fig. 2. Burning shrinkage for samples T1, T2 and T3

Upon burning of formative mixtures out of low-melting illite clays, one can get the sintered ceramic material with density >2000 kg/m^3, water absorption <5 %, however, the temperature of burning of such mixtures is higher than 1100 ºC [15, 19]. The densities data for the samples T1, T2 and T3 are provided in Figs. 3 and 4. One can see that the average values of density do not practically differ for the samples T1, T2 and T3 when burnt at temperatures of 950, 1000 and 1040 ºC. The dynamics of density change at a temperature higher than 1040 ºC. The comparative data analysis shows that upon burning of samples at 1060 ºC, the density of obtained sintered ceramic body increases from 1995 kg/m^3 (Sample T3) to 2097 kg/m^3 (Sample T2). It was found out that the maximal average density of sintered ceramic body for the samples T3 (2160 kg/m^3) was received upon burning of samples at temperature of 1080 ºC (Fig. 3). The water absorption data for the burnt samples T1, T2 and T3 are provided in Fig. 4. As concerns samples burnt at 1040 ºC, after addition of 25 % milled nepheline syenite, the average water absorption decreases from 9.6 % (Sample T3) to 6.5 % (Sample T2). In event of burning of these samples at temperature of 1060 ºC, the average water absorption decreases from 5.2 % to 2.5 %. The comparative data analysis discloses that the value of water absorption for the samples T1 and T2 burnt at 1040 ºC makes 7.7 % and 6.5 %, respectively.

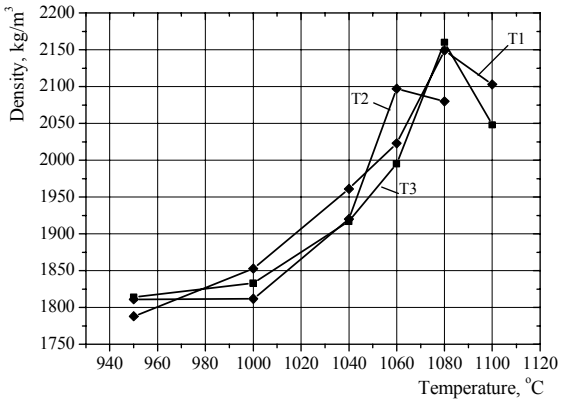

Fig. 3. Density of the samples T1, T2 and T3 versus burning temperature

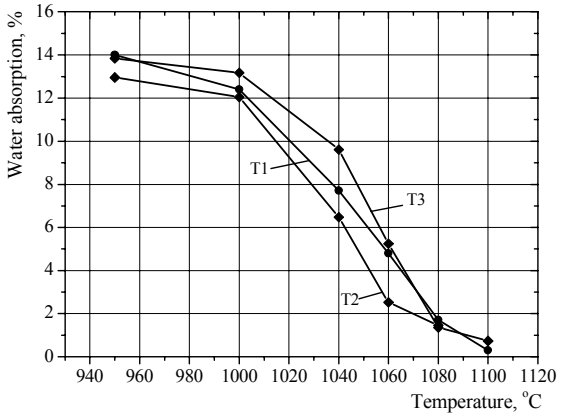

Fig. 4. Water absorption for the samples T1, T2 and T3 versus burning temperature

The measurements of ultrasonic pulse velocity in the sample and analysis of its change characterize the structural parameters of the sintered ceramic material [20], as well as consistent patterns of formation of minerals in

the aluminosilicate systems [21]. Ultrasonic pulse velocity analysis data for the samples T1, T2 and T3 are provided in Fig. 5. By virtue of ultrasonic testing of burnt samples T3 and T1, we can maintain that the addition of 10 % milled nepheline syenite into mixture results in higher values of ultrasonic pulse velocity within interval of temperatures from 950 ºC to 1100 ºC (Fig. 5). It was measured that the value of ultrasonic pulse velocity for the sample T2 burnt at 1060 ºC decreased from 4025 m/s (Sample T1) to 3515 m/s. The comparative analysis of X-ray diffraction and ultrasonic pulse velocity data clarified that the appearance of new formations: leucite and aegirine, during burning accounts for the decrease in value (Figs. 5 and 8).

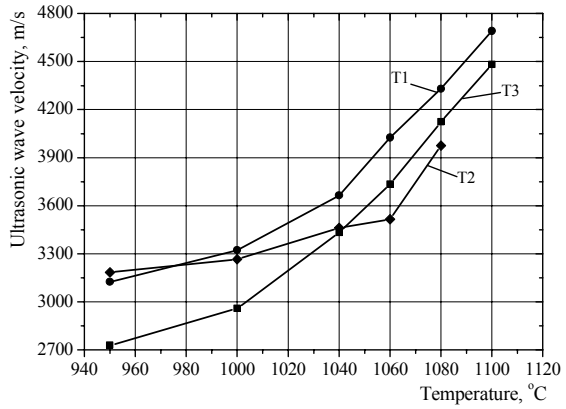

Fig. 5. Ultrasonic pulse velocity data for the samples T1, T2 and T3

The dilatometric methods helped to inquire into the mechanism of processes running in the course of sintering of formative mixtures T1, T2 and T3. The results of investigations are provided in Fig. 6. Analyzing these results, one's eye is caught by the fact that at heating of samples T3 and T1, the commencement of local liquid phase origination is marked by sharp change in length of sample under investigation at temperature of 830 ºC.

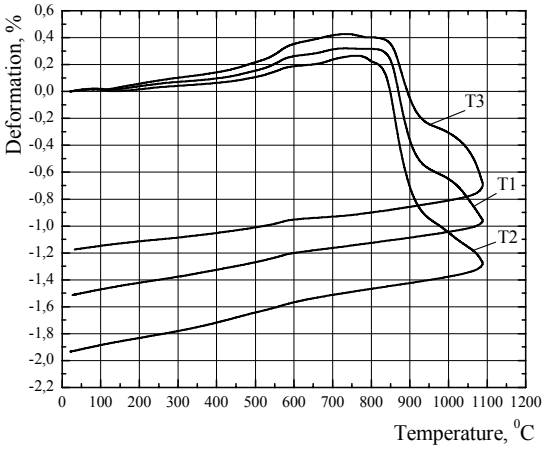

Fig. 6. Dilatometric data for samples T1, T2 and T3

The investigation of shrinking deformations of the formative mixtures with nepheline syenite additive showed that nepheline syenite decreases the viscosity of the liquid phase [6]. Therefore, upon addition of 25 % nepheline syenite additive to low-melting illite clay (Sample T2), the start temperature of local liquid phase formation decreased from 830 ºC to 800 ºC. At 1070 ºC length increased from 0.96 % (Sample T1) to 1.27 % (Fig. 6, Sample T2).

The processes of decomposition, appearance of new formations and their crystallization, which occur in the course of heating of samples T1 and T2, were investigated employing differential thermal analysis and X-ray diffraction. The results are provided in Figs. 7 and 8.

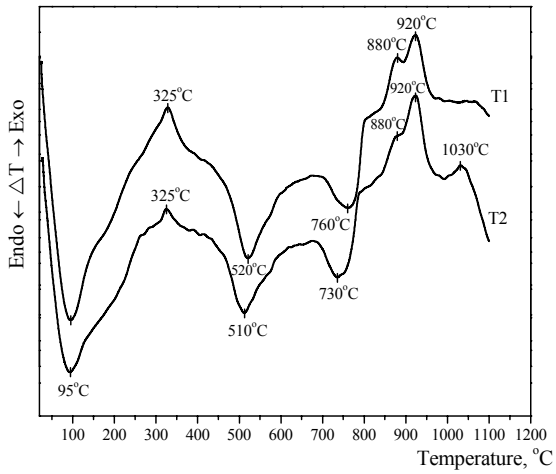

Fig. 7. Thermographic data for formative mixtures T1 and T2

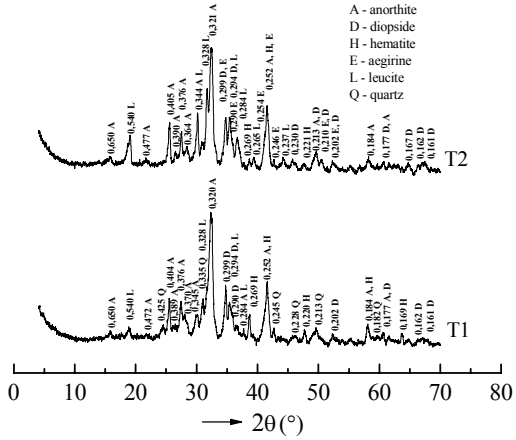

Fig. 8. X-ray diffraction patterns for formative mixtures T1 and T2 burnt at temperature of 1070 ºC

The processes going on in formative mixtures during their burning are characterized by dehydration and decarbonization processes of low-melting illite clay [15] and the ions Na^+ present in the composition of fluxing additives react actively with minerals of clay [22]. The analysis of curve DTA for the formative mixture T1 indicates that the first maximum of endothermal effect, fixed at 95 ºC, describes the process of release of adsorption water and that within range of temperatures from 410 ºC to 660 ºC the dehydration of hydromicas contained in clay takes place (Fig. 7). When the temperature reaches 760 ºC, the third maximum of endothermal effect is observable. This effect depicts the process of decomposition of clay-contained carbonates ($CaCO_3$ and $MgCO_3$) and formation of free oxides of calcium and magnesium (CaO and MgO) [16]. It was established that within interval of temperatures from 840 ºC to 970 ºC (the maximums of exothermal effects being at 880 ºC and 920 ºC) one can observe the reaction of CaO and MgO with aluminosilicate compounds contained in clay.

The X-ray diffraction analysis demonstrated the formation of anorthite ($CaAl_2Si_2O_8$) and diopside ($CaMgSi_2O_6$) at crystallization of reaction products, as well as the formation of hematite (Fe_2O_3) at crystallization of clay-contained iron compounds (Fig. 6, Formative Mixture T1) takes place. In the formative mixture T2 with percentage of nepheline syenite increased from 10 % to 25 % the maximal temperature of endothermal effect decreased from 760 ºC to 730 ºC and that of exothermal effect was observed at 1030 ºC (Fig. 5). The data of X-ray diffraction investigations show that this exothermal effect can be explained by the reaction of the ions Na^+ and K^+ present in the composition of nepheline syenite with the aluminosilicate compounds contained in clay. It was found out that during the crystallization of reaction products, leucite ($KAlSi_2O_6$) and aegirine $NaFe(Si_2O_6)$ are formed.

CONCLUSIONS

The study investigates formative mixtures with added fluxing material: nepheline syenite. The effect of this additive on properties of sintered ceramics is analyzed. The fluxing effect of nepheline syenite is observed in the formative mixture with added 10 % of ground nepheline syenite, the specific surface of which is 8200 cm^2/g and the average diameter of grist particles is 9.79 μm. The dilatometric investigations showed that along with increase of content of ground nepheline syenite in the formative mixture from 10 % to 25 %, the start of formation of local liquid phase is observed at 800 ºC, while the change in length at 1070 ºC increased from 0.96 % to 1.27 %. By the thermographic investigations, it was established that the temperature of maximal endothermic effect, which characterizes disintegration of carbonates contained in clay, decreased from 760 ºC to 730 ºC. After burning of the formative mixture with added 25 % of ground nepheline syenite, at 1060 ºC the sintered ceramic material was received, and its density was 2097 kg/m^3 and its water absorption of 2.5 %, and, as to burning shrinkage within interval from 950 ºC to 1060 ºC, it is characterized by higher values than those of the formative mixture with added 10 % of ground nepheline syenite.

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