LOW-EXPANDING CERAMICS BASED ON FERROUS CORDIERITE

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In the field of development of technical ceramics, the problem of creating highly heat-resistant and wear-resistant ceramic materials that can be used in machine-building, electronic, chemical, light and other industries is an urgent issue.Industrial production of such materials is currently absent in the republic, and products manufactured by individual enterprises from heat-resistant and wear-resistant ceramics are inferior in their operational and economic characteristics to foreign analogues.In the manufacture of high-temperature ceramics, low-expansion phases are used, supplementing them with other structural components to regulate the heat resistance criteria [1, 2].

The system $FeO–Al_2O_3–SiO_2$ is not of particular interest for the production of refractory materials due to the content of low-melting eutectics; however, it can be used as a basis for the synthesis of heat-resistant technical materials with increased strength and wear resistance. Information about this system and its features, which consist in the formation of a low-expanding ferrocorderite phase, as well as on the synthesis of ceramic materials with a low thermal expansion coefficient ($1.8–2.4 \cdot 10^{-6}$ K^{-1}) are rather limited and are presented in [3, 4]. The greatest activity to the occurrence of reactions at lower temperatures is manifested in iron (II) (wustiteFeO) compared to Fe_2O_3, as evidenced by the data [5]. Ferrocordieriteis formed at lower temperatures compared to ordinary magnesium cordierite, which is of particular interest in the study of this system. It was revealed that iron takes an active part in sintering and the formation of iron-containing crystalline phases (hercynite – $FeO \cdot Al_2O_3$, ferrocordierite – $2FeO \cdot 2Al_2O_3 \cdot 5SiO_2$ and magnetite – Fe_3O_4), forming low-viscosity melts.

Thus, the purpose of this work is to conduct research in the field of synthesis of ceramic materials for technical purposes based on the

$FeO–Al_2O_3–SiO_2$ system, which will make it possible to level out the disadvantages of traditional cordierite ceramics. The main objectives of the study are the synthesis of samples of ceramic materials in the $FeO–Al_2O_3–SiO_2$ system, the study of their physicochemical and thermomechanical characteristics, the determination of the effect of synthesis temperature and the number of initial components on the properties of the samples, the study of behavior during heating, features of phase formation and formation composition.

The materials were synthesized in a wide area of the three-component system $FeO–Al_2O_3–SiO_2$ in the field of crystallization of ferrocordierite. The content of FeO for the field of compositions of the initial mixtures varied from 15 to 25 wt. %, Al_2O_3– from 40 to 50 wt.%, SiO_2 – from 40 to 50 wt.%. The laboratory samples synthesized at different firing temperatures had a regular geometric shape with no signs of burnout and were characterized by a fine-grained dense structure. Depending on the quantitative content of iron (II) oxide, the color of the samples changed from light gray (composition No. 3, 6 and 9), gray (composition No. 2, 5 and 8) to dark gray (composition No. 1, 4 and 7) in which the content of FeO maximum. The Table 1 shows the indicators of the properties of prototypes at different firing temperatures.

Table 1. **Indicators of the properties of prototypes at different firing temperatures**

Composition number	Indicators of properties, firing temperature, °C								
	ρ_{per}, kg/m^3	W, %	P_{op}, %	ρ_{per}, kg/m^3	W, %	P_{op}, %	ρ_{per}, kg/m^3	W, %	P_{op}, %
	1100			1150			1200		
1	2310	7.91	18.29	2440	5.39	13.16	2590	3.39	8.78
2	2220	8.17	18.15	2310	7.32	16.92	2470	3.52	8.72
3	2080	12.66	26.37	2240	9.55	21.43	2460	4.12	10.14
4	2310	8.76	20.50	2460	6.47	15.91	2600	3.81	9.88
5	2210	10.27	22.69	2410	8.31	19.72	2610	4.56	9.29
6	2100	11.31	23.75	2230	8.91	19.92	2550	5.26	13.41
7	2310	9.61	22.22	2300	7.04	16.06	2580	4.50	11.64
8	2210	11.68	25.78	2240	8.36	21.11	2550	4.63	11.84
9	2110	11.81	24.89	2190	9.08	21.43	2420	3.36	8.50

The minimum values of water absorption and open porosity are characterized by samples with a maximum firing temperature. As the FeO content increases and, accordingly, the refractory Al_2O_3 oxide itself decreases, the apparent density increases significantly due to the formation of a larger amount of melt during sintering, as well as the active formation of iron-containing crystalline phases in the studied region of the $FeO–Al_2O_3–SiO_2$ system.

The study of thermal expansion of prototypes in conjunction with the initial composition and firing temperature shows their complex dependence. The wide range of TCLR values of the samples (6.46–$3.60 \cdot 10^{-6}$ K^{-1}) at a measurement temperature of 300 °C is determined by the different ratios of the highly expanding quartz component, the crystalline phase of ferrocorderite, and the resulting glassy phase. Table 2 presents the values of TCLR of samples of ceramic materials depending on the temperature of their synthesis.

Table 2. **TKLR values of prototypes of ceramic materials**

Temperature roasting, °C	Sample number, TCLR, $\alpha \cdot 10^{-6}$ K^{-1}								
	1	2	3	4	5	6	7	8	9
1100	4.46	4.45	5.17	5.14	5.48	6.40	5.37	6.10	6.46
1150	4.12	4.05	4.78	4.67	5.35	5.84	4.98	5.68	6.08
1200	3.87	3.60	4.31	4.10	4.98	5.54	4.55	5.17	5.68

With an increase in the FeO content, the TCLR indexes decrease due to an increase in the fraction of the released low-expansion ferrocorderite phase in the structure of the sintered material. Composition No. 2, which is closest to the point of crystallization of the ferrous cordierite phase, is characterized by the minimum TCLR value ($3.6 \cdot 10^{-6}$ K^{-1}). An increase in the firing temperature to 1200 °C leads to a decrease in thermal expansion coefficient for all the studied compounds, which is due to the intense release of ferrocordierite, as well as a decrease in the amount of quartz component. The highest values of TCLR for samples of compositions No. 6 and 9 are characteristic of samples with the lowest FeO content, which is probably determined by the formation of other higher-expanding aluminosilicate phases.

Table 3 shows the average values of indicators of mechanical strength of prototypes at various temperatures of synthesis.

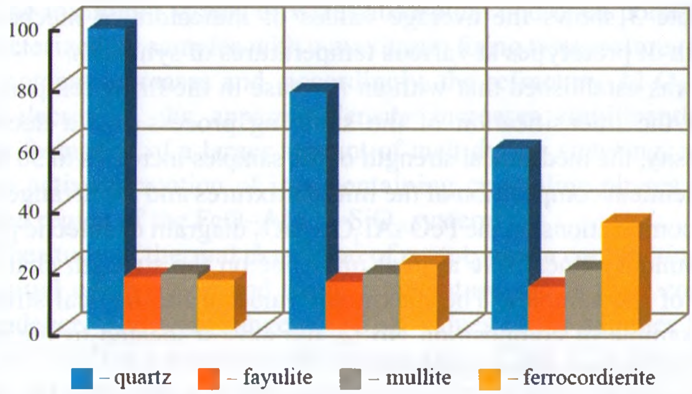
It was established that with an increase in the firing temperature due to the intensification of the sintering process and a decrease in porosity, the mechanical strength of the samples increases to 50 MPa. The chemical composition of the initial mixtures and the arrangement of the compositions on the $FeO–Al_2O_3–SiO_2$ diagram of eutectic points and boundary lines have a great influence on the strength characteristics of the samples. The maximum value of mechanical strength has a sample of composition No. 2, the closest located to the point of crystallization offerrocorderite.

Table 3. **Mechanical flexural strengths**

Temperature roasting, °C	Sample number, flexural strength, MPa								
	1	2	3	4	5	6	7	8	9
1100	30.3	32.2	26.9	32.1	27.1	21.1	34.8	30.3	24.8
1150	35.1	38.1	32.2	36.4	30.2	23.9	37.1	32.2	26.5
1200	47.4	50.3	43.6	49.7	35.7	29.8	41.1	35.2	30.5

The study of thermal effects occurring during heating of the initial mass of the optimal composition No. 2 was carried out using differential thermal analysis. An analysis of the DTA curve indicates the presence of a first poorly pronounced endo-effect with a maximum in the temperature range of 60–70 °C, due to the removal of a small amount of physical moisture sorbed by clay minerals. The second intense endothermic effect with a maximum at 520 °C is caused by the release of chemically bound water from clay minerals with the formation of a metakaolinite, followed by its subsequent destruction (partial amorphization). The only exothermic effect in a narrow temperature range with a peak at 970 °C is characterized by a rearrangement of the metakaolinite lattice with a transition amorphized to a cryptocrystalline structure and possible polymorphic transformations, as well as the primary process of ferrocardierite formation.

The study of samples of ceramic materials of mass compositions No. 2, synthesized in the temperature range of 1100–1200 °C, using



The dependence of the intensities of diffraction maxima crystalline phases in samples of composition No. 2 on sintering temperature

X-ray phase analysis method shows a close relationship between the properties of ceramics and its phase composition. Figure shows the dependence of the intensities of the diffraction maxima of the extraction of crystalline phases in samples of composition No. 2 on the sintering temperature.

It was determined that the phase composition of the materials under study is polymineral and is represented by quartz (SiO_2), fayalite ($2FeO·SiO_2$), mullite ($3Al_2O_3·2SiO_2$) and ferrocordierite ($2FeO·2Al_2O_3·5SiO_2$) with predominant prevalence of carciferous composition. The formation of such a phase as fayalitecan be explained by the possible interaction of unreacted wustite with the formed silica during the decomposition of the clay component.

Sample No. 2, annealed at a temperature of 1100 °C, identifies all of the listed crystalline phases, however, with a further increase in the firing temperature to 1200 °C, the content of the ferrocordierite phase increases, which will affect the decrease in thermal expansion coefficient of the synthesized samples. Additional phases are fayalite, mullite and residual crystalline quartz. With an increase in the sintering temperature, the relative amount of the crystalline phase of quartz decreases, since it is partially dissolved in the melt, and partly goes to the formation of other phases. In the process of increasing the temperature of synthesis, the amount of formed mullite slightly increases, and the crystalline phase of fayalite becomes slightly smaller.

It was established that based on the $FeO–Al_2O_3–SiO_2$ system, mechanically strong heat-resistant materials with a low calcination temperature were obtained. The material No. 2 synthesized at 1200 °C has the best physicochemical properties: water absorption – 3.52 %; apparent density – 2470 kg/m^3; thermal expansion coefficient – $3.6 \cdot 10^{-6}$ K^{-1}; mechanical strength in bending – 50.3 MPa; acid resistance – 97.55 %, alkali resistance – 98.71 %; Mohs hardness – 7; heat resistance (800 °C – water) – 90 heat cycles; thermal conductivity coefficient – 0.79 W/(m·K). The phase composition of the material is represented by ferrous cordierite, mullite, fayalite and quartz.

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