Advanced Anorthite Lightweight Castables for Carbon-Containing Atmosphere Application

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Heat insulating refractories have been widely adopted owing to the low thermal conductivity that permit reducing heat losses through the lining of furnaces, to reduce a consumption of energy carriers in thermal units. Use of heat insulating castables allows executing lining in places where its performance by shaped refractories is impossible. Two types of heat insulating castables based on anorthite microporous aggregate with an apparent density of 0,8 g/cm^3 and 1,3 g/cm^3 are developed, the possibility of their use in carbon-containing atmospheres at temperatures up to 1200 °C is established. Phase formation in the castable matrixes is studied, as well as the formation of secondary anorthite in the matrix is established that promotes resistance of the castable to carbon-containing atmosphere influence.

1 Introduction

In the conditions of continuous increase in prices for energy resources the heat insulating refractories application in thermal units of various industries has great value as allows to reduce significantly heat losses through the lining of the units, and, therefore, to reduce a consumption of energy carriers [1]. Effectiveness and economy of the thermal unit operation and manufacturing processes are directly bound with lining thermal isolation for which the thermal conductivity of applied materials is defining quality indicator. In a number of places, the thermal units lining cannot be executed by shaped refractories, but monolithic lining from heat insulating castable can be realised. Therefore, the production technology development of high-performance heat insulating castable with ultralow thermal conductivity is an actual task.

In world practice anorthite refractory products which thanks to the low iron oxides content can serve both in oxidizing and in reducing atmospheres are widely used, at the same time they have high thermal insulating properties [2, 3]. The purpose of this work is a development of anorthite heat insulating castable for application in carbon-containing atmospheres.

Tab. 1 Chemical composition of alumina silicate raw materials

Material	Content [mass-%]							
	L.o.I	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	CaO	MgO	R_2O
Clay component	13,5	37	47,4	0,65	0,62	0,61	0,22	traces
Chamotte	0,84	45,4	49,3	1,44	1,82	0,9	0,15	0,15
FGNAS	0,34	60,4	34,9	2,4	1,02	0,64	0,24	0,02

2 Manufacturing of anorthite aggregates

2.1 Experimental part

For a research on manufacturing of anorthite aggregates raw materials were used: clay component, chamotte, fine-grained natural alumina silicate (FGNAS), calcium-containing component. Chemical composition of the alumina silicate raw materials is given in Tab. 1.

From the raw materials slips were prepared and samples were casted, then green was dried in an electric drying chamber at a temperature no more than 100 °C and fired in the electric furnace at temperatures of 1250 and 1300 °C.

2.2 Results and discussion

Researches on a selection of the optimum material composition of the anorthite aggregates were carried out on samples with the stoichiometric oxides amount which is necessary for anorthite formation. It was established, that the optimum CaO content in products has to make ~15 %. Some de-

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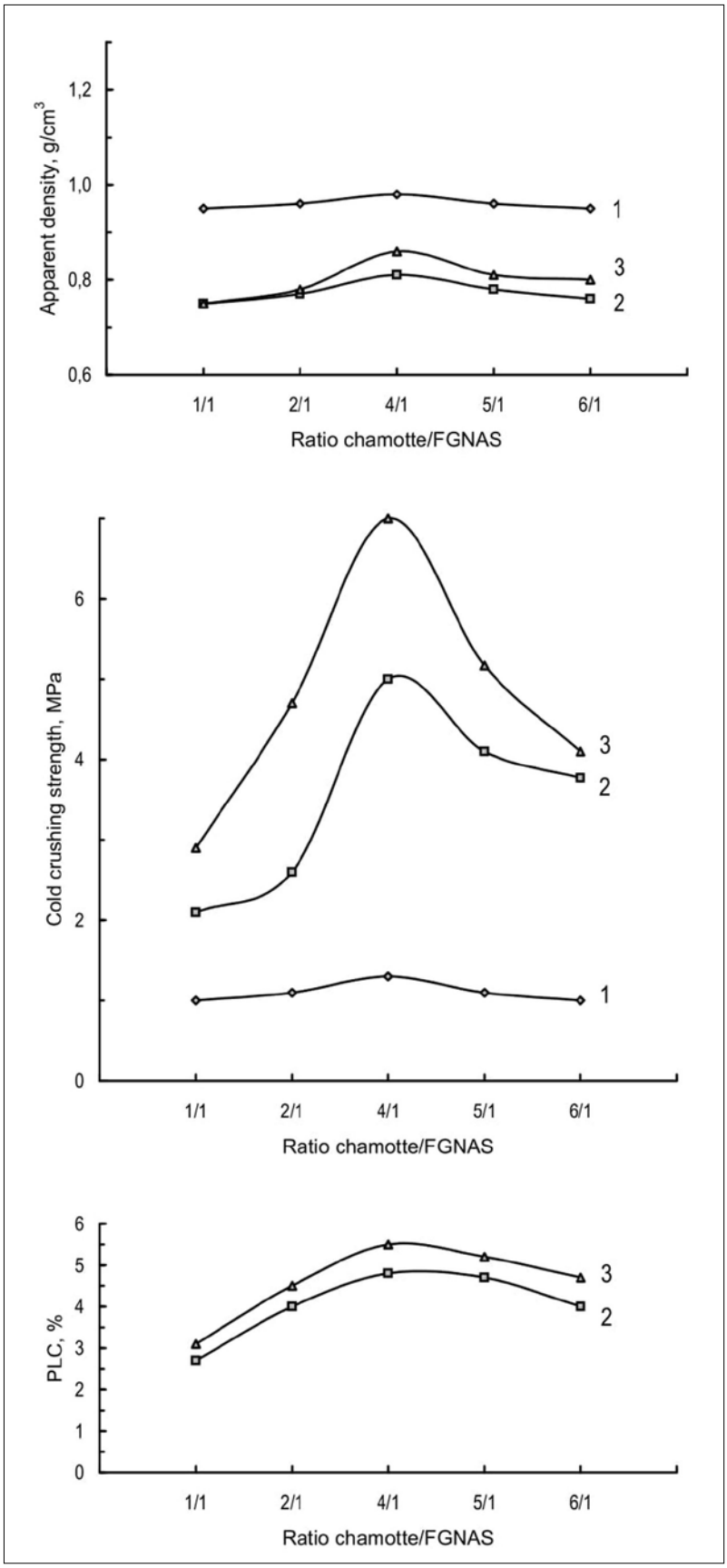

Fig. 1 Dependence of anorthite aggregates properties on a ratio of chamotte and FGNAS in batch [4]: numbers at curves: 1 – green; 2 – firing at 1250 °C; 3 – firing at 1300 °C

crease of CaO amount from stoichiometric to the area of more refractory compositions prevents a possibility of the low-temperature phase's formation lowering refractoriness and classification temperature. Ratio influence of the FGNAS additive in combination with chamotte was studied. Researches results of samples properties are shown in Fig. 1.

As shown in Fig. 1, a deviation from the ratio of chamotte to FGNAS from 4/1 both to the larger party, and to smaller leads to decrease in apparent density of samples from 0,80–0,84 g/cm^3 to 0,75–0,79 g/cm^3. It is caused by formation of new phases with volume increase, such as mullite also anorthite. At the same time, the linear shrinkage decreases from 4,8–5,5 to 3,0–4,6 % and samples strength somewhat decrease from 5–7 MPa to 2–4 MPa. Increase in firing temperature up to 1300 °C leads to some increase in strength, and apparent density at the same time practically does not change and is 0,75–0,81 g/cm^3.

The difference in the dependence character of samples properties of various compositions is caused by a processes complex happening at firing and affecting on structure formation of material. So, removal of physically and chemically combined water in the clay component happens with volume decrease which is interfered by frame structure of green. Processes mullite formation and interaction of alumina silicates with CaO leading to anorthite formation, as well as secondary mullite synthesis in chamotte, happen with volume increase. Liquid-phase sintering, due to formation of the eutectic multicomponent melts in the presence of alkalis and iron, happens with volume decrease. All these transformations in the structure lead to changes in strength and density values of materials at various stages of firing.

On the basis of carried out researches the anorthite aggregates composition which was used later for manufacturing of heat insulating castable has chosen. Properties and phase composition of aggregates are given in Tab. 2.

Thermal conductivity of the received aggregates is significantly lower than traditional refractory heat insulating materials and approaches to thermal conductivity of ceramic fibre products. Such low thermal conductivity is explained by a microporous structure

of the aggregates; the prevailing pore size makes 1–6 µm [5].

Thus, the manufacturing technology of anorthite aggregates with a microporous structure is developed. This technology includes the following procedures: raw materials preparation; mix preparation; mix casting in metal multi-section moulds; green drying; products firing. Unlike traditional production in the developed technology, the burning-out additives and foam are not used, and a pore agent is a water withheld in green structure and providing micropores formation at stages of drying and firing of products.

3 Manufacturing of heat insulating castable

3.1 Experimental part

For carrying out researches as initial components the microporous anorthite aggregates with specially selected fractional composition and the maximal grain size of 5 mm, as well as high-alumina cement by own production with a specific surface of 6100 cm^3/g were used. As additives an expanded perlite and fine-grained natural alumina silicate (FGNAS) with the prevailing grain size of 8–40 µm were applied.

The chemical analysis of the used raw materials is presented in Tab. 3.

The additives of expanded perlite and FGNAS were used in a marketable condition without additional processing. The additives amount was varied within the dedicated area on diagram (Fig. 2), and the high-alumina cement amount in all compositions is constant.

Components were mixed in dry, then water was added and from received mixes the samples were formed by ramming, vibration forming and semi-dry pressing methods in the form of cubes with an edge of 50 mm and bricks of 230 mm × 115 mm × 65 mm in size. The moisture was selected individually for each mix on its workability. After formation, the samples were cured in the wet conditions (relative humidity of air >90 %) within 7 days and dried in a drying chamber at a temperature of 110 °C to constant weight, and then properties of the castables were defined. The samples after moist curing and drying also were fired at temperatures of 1200 °C and 1300 °C for 2 h.

Properties of the samples were determined according to the standard methods. Thermal conductivity was determined by the

Tab. 2 Properties and phase composition of anorthite aggregates

Characteristic	
Content [mass-%]	
SiO_2	42,5
Al_2O_3	39
CaO	15,1
Fe_2O_3	0,75
L.o.I. [%]	0,44
Phase content [vol.-%]	
Anorthite	74–77
Quartz	traces
Kyanite + sillimanite	1–2
Mullite + glass	16–20
Chamotte	3–4
Accessory minerals	1–3
Samples properties	
Apparent density [g/cm^3]	0,8
Cold crushing strength [MPA]	6
Linear shrinkage at firing [%]	4,8
Classification temperature [°C] (additional shrinkage ≤1 %)	1300

Tab. 3 Chemical composition of raw materials*

Material	**Content [mass-%]**								
	L.o.I. [%]	**SiO_2**	**Al_2O_3**	**TiO_2**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**
Microporous anorthite aggregates	0,16	38,6	42,3	1,26	0,78	16,2	0,88	not deter.	not deter.
High-alumina cement	0,52	1,09	76,1	–	0,39	21,9	–	–	–
Perlite	1,28	75,34	12,84	0,07	2,82	1,67	0,44	1,64	3,9

*Chemical composition of FGNAS is given in Tab. 1

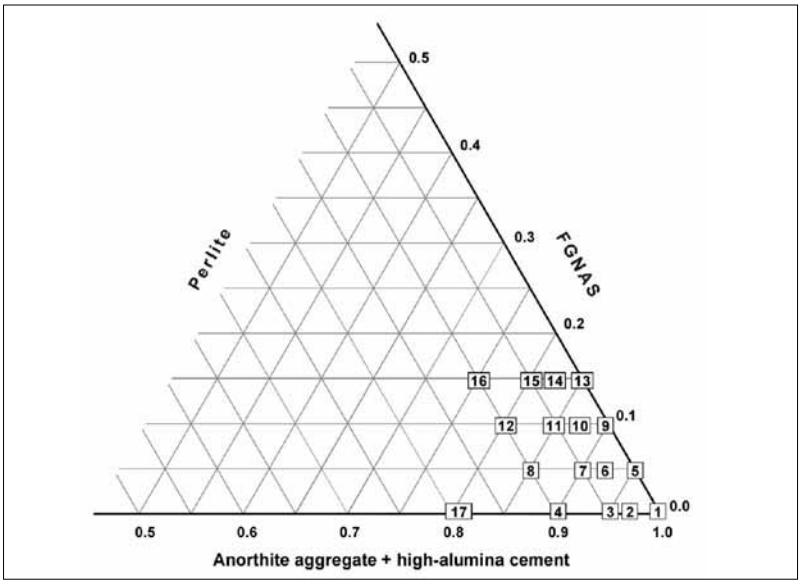

Fig. 2 Compositions of experienced heat insulating castable

Tab. 4 Properties of castable samples based on anorthite microporous aggregates with perlite additive

Composition Number	Time of Moist Curing [d]	Temperature of Thermal Treatment [°C]	Apparent Density [g/cm³]	CCS [MPa]	PLC [%]
1	7	–	1,41	8,2	–
		1200	1,24	6,3	0,9
		1300	1,26	7,8	1,3
2	7	–	1,29	6,3	–
		1200	1,15	5,2	0,8
		1300	1,17	5,7	1,5
3	7	–	1,28	5,7	–
		1200	1,1	4,6	0,9
		1300	1,13	4,9	1,8
4	7	–	1,16	4,8	–
		1200	1,02	3,4	0,8
		1300	1,03	3,6	1,9
17	7	–	0,83	2,5	–
		1200	0,72	1,7	1,2
		1300	0,74	2	2

Tab. 5 Properties of castable samples based on anorthite microporous aggregates with FGNAS additive

Composition Number	Moist Curing Time [d]	Temperature of Thermal Treatment [°C]	Apparent Density [g/cm³]	CCS [MPa]	PLC [%]
1	7	–	1,41	8,2	–
		1200	1,24	6,3	0,9
		1300	1,26	7,8	1,3
5	7	–	1,48	8,4	–
		1200	1,25	5,8	0,7
		1300	1,28	7,8	1,6
9	7	–	1,45	8,1	–
		1200	1,28	5,8	0,7
		1300	1,3	6,7	1,3
13	7	–	1,50	7,4	–
		1200	1,29	4,6	0,5
		1300	1,30	7	0,9

constant flow method in accordance with GOST 12170 on the samples with the size of 114 mm × 114 mm × 65 mm.

3.2 Results and discussion

The perlite additive influence research on properties of the castable samples showed that, after 7 days of moist curing and drying with increase in the perlite amount decrease both apparent density from 1,41 g/cm³ (without additive) to 0,83 g/cm³ (with maximal perlite amount) and cold crushing strength from 8,2–2,5 MPa, and it is quite naturally (Tab. 4). The dependence character of samples properties on the perlite amount remains and at its maximal contents at a temperature of 1200 °C: apparent density decreases to 0,72 g/cm³, cold crushing strength reaches 2,0 MPa, and shrinkage makes 1,2 % that allows using such castable at temperatures up to 1200 °C (composition 17). Increase of firing temperature to 1300 °C leads to increase in shrinkage up to 2 %, and it is critical.

For a purpose of using temperature increase of the castables based on anorthite microporous aggregates, an influence of FGNAS additive on properties of the samples was investigated. Properties of the castable samples with FGNAS additive after moist curing and thermal treatment are given in Tab. 5.

As shown in Tab. 5, apparent density and strength of the castables based on anorthite microporous aggregates both with FGNAS additive and without additive (composition 1), increases with time of moist curing and by 7 days lie in the range of 1,4–1,5 g/cm³ and ~8 MPa respectively. After firing at 1000 °C the apparent density decreases for all compositions as a result of hydrates decomposition in the cement. With temperature increase, it does not change, but somewhat increases with increase in FGNAS additive amount up to 1,3 g/cm³. With temperature increase cold crushing strength increases to 7–8 MPa, the samples shrinkage after firing at 1300 °C makes 1,3–1,6 %, and only at the maximum amount of FGNAS additive decreases to 0,9 % that is bound to a process of mullite formation in alumina silicate.

For decrease in apparent density combined adding of the perlite and FGNAS in the castable composition was tested. The received results are given in Tab. 6.

Tab. 6 shows that with increase in the perlite amount in mix composition both apparent density and cold crushing strength after 7 days of moist curing naturally decreases. The sample of composition 15 at the apparent density of 1,3 g/cm³ has the good strength of 5,5 MPa. Thermal treatment of the samples at temperatures of 1000–1300 °C showed that the perlite additive promotes to increase in the samples strength without their apparent density change, which is bound to the beginning of sintering action of a small perlite amount and mullite formation from alumina silicate, interfering of material shrinkage.

After firing at 1300 °C the samples shrinkage is 0,9–1,0 % that shows a possibility of such castable using at temperatures up to 1300 °C.

Thus, on a complex of properties "apparent density – strength – shrinkage" the compositions 17 with apparent density of 0,8 g/cm³ and 15 with apparent density of 1,3 g/cm³ (later CA-0,8 and CA-1,3 respectively) were chosen. Properties of the developed castables are given in Tab. 7.

The castable formation method has significant effect on the strength of heat insulating castable products based on anorthite microporous aggregate. It is established that it is possible to receive with vibroformation method the heat insulating anorthite castable, characterised by strength in ~2 times more at the same apparent density, in comparison with castable produced by ramming method.

4 Properties of heat insulating castable based on anorthite microporous aggregate after thermal treatment in carbon-containing atmosphere

For properties research of the heat insulating castable based on anorthite microporous aggregate after thermal treatment in the carbon-containing atmosphere, the samples were placed in corundum crucibles, pouring layer by layer cryptol to the top edge of a crucible. The crucibles were densely closed corundum covers, and then joints of the cover and edge of the crucible were covered with alumina, moistened by orthophosphate acid, for sealing. Crucibles with the samples were placed in a furnace with carbide silicon heaters. They had thermal treatment at 1200 °C for 20 h, 50 h and 80 h. The samples properties of the anorthite heat insulating castables before their thermal treatment in the carbon-containing atmosphere are given in Tab. 8.

As shown from Tab. 8, the samples before their thermal treatment in the carbon-containing atmosphere have rather high strength at low values of apparent density and low thermal conductivity. It is established that after thermal treatment in the carbon-containing atmosphere restoring of SiO_2 is not observed (chemical composition of the samples remains almost invariable). In the castables samples after thermal treatment in the carbon-containing atmosphere, there is a slight amount of carbon (up to 0,07 %). Properties of the samples after their thermal treatment in the carbon-containing atmosphere are given in Tab. 9.

Tab. 9 shows that after thermal treatment in the carbon-containing atmosphere the apparent density and strength decrease that is characteristic also of the samples, thermally treated on air. Decrease of apparent density and strength is explained by a dehydration of cement binder, being a part of the castables. With increase in exposure time at thermal treatment in the carbon-containing atmosphere from 20–80 h the apparent density, strength and shrinkage of the samples of both brands are practically left without changes [7].

Tab. 6 Properties of castable samples based on anorthite microporous aggregates with perlite and FGNAS additives

Composition Number	Time of Moist Curing [d]	Temperature of Thermal Treatment [°C]	Apparent Density [g/cm³]	CCS [MPa]	PLC [%]
13	7	–	1,5	7,4	–
		1200	1,29	4,6	0,5
		1300	1,3	7	0,9
14	7	–	1,39	7	–
		1200	1,2	4,3	0,5
		1300	1,23	5,3	0,9
15	7	–	1,3	5,5	–
		1200	1,12	3,9	0,6
		1300	1,13	4,3	1
16	7	–	1,16	4	–
		1200	1,02	1,8	0,5
		1300	1,04	4,3	1,1

Tab. 7 Properties of castables [6]

Characteristics	Brand	
	CA-0,8	CA-1,3
Content [mass-%] (without L.o.I.):		
Al_2O_3	50,1	57,2
CaO	15,6	15,4
SiO_2	31	24,9
Fe_2O_3	1,05	0,77
Apparent density [g/cm³] after:		
drying at 110 °C	0,83	1,28
firing at 1000 °C	0,74	1,12
Cold crushing strength [MPa] after:		
7 days of moist curing	2,56	5,54
firing at 1000 °C	1,98	3,9
Thermal conductivity [W/(m·K)] at average temperature of 350 ± 25 °C	0,16	0,21
PLC [%] after firing for 5 h at temperature	1200 °C	1300 °C
	–1,8	–1,2

Tab. 8 Properties of samples before thermal treatment in the carbon-containing atmosphere

Sample	Time of Moist Curing [d]	Temperature of Thermal Treatment [°C/h]	Apparent Density [g/cm³]	CCS [MPa]	PLC [%]	λ, [W/(m·K)] at Average Temperature 350 / 650 / 850 °C
CA-1,3	7	–	1,28	6,8	–	0,274 / 0,298 / 0,336
		1000/2	1,08	5,2	0,4	
		1200/5	1,10	5,9	0,6	
CA-0,8	7	–	0,79	2,6	–	0,162 / 0,201 / 0,237
		1000/2	0,70	2,0	0.8	
		1200/5	0,71	2,2	1,2	

Tab. 9 Samples properties after thermal treatment in the carbon-containing atmosphere at a temperature of 1200 °C with various holding times

Sample	Holding Time at Thermal Treatment in the Carbon-Containing Atmosphere [h]	Properties of Samples		
		Apparent Density [g/cm³]	CCS [MPa]	PLC [%]
CA-1,3	20	1,09	5,8	0,1
	50	1,08	5,1	0,1
	80	1,10	5,9	0,3
CA-0,8	20	0,69	2,0	1,2
	50	0,71	1,8	1,1
	80	0,71	2,4	1,3

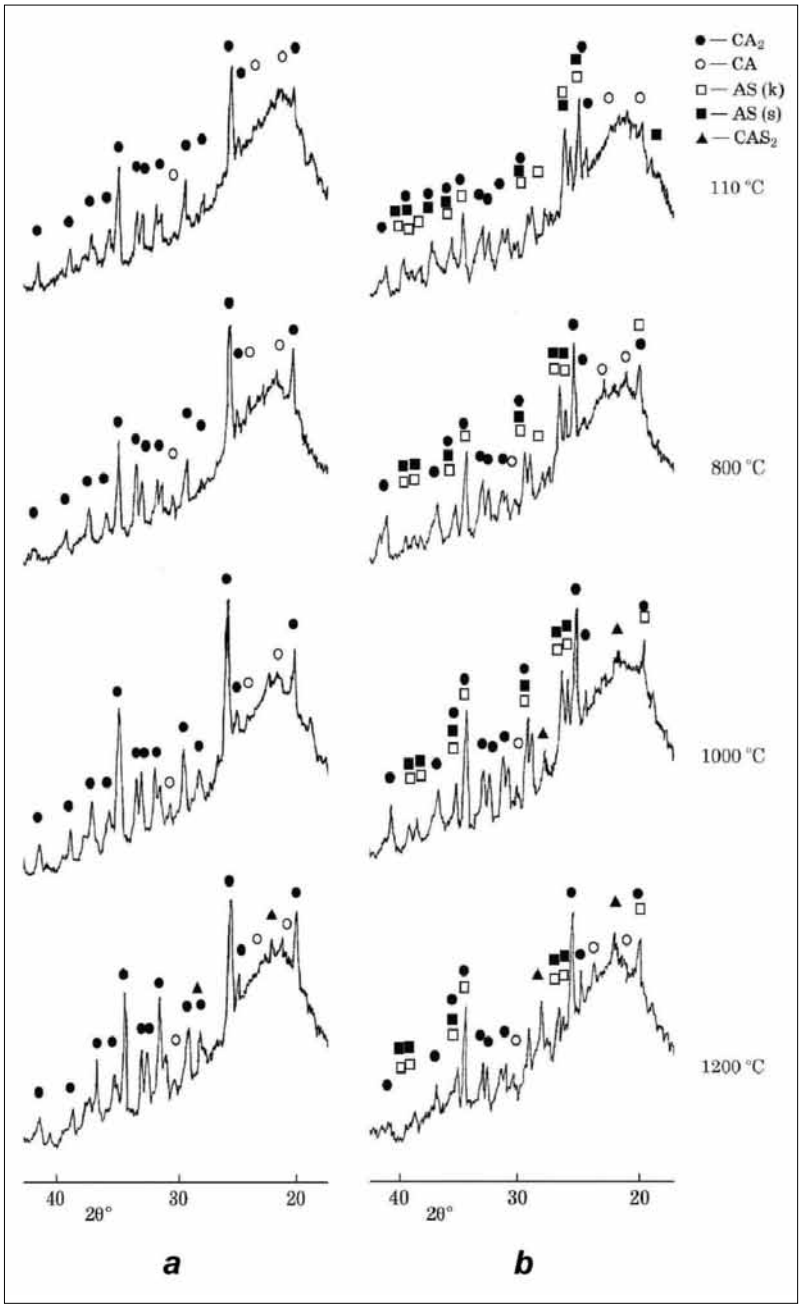

Fig. 3 a–b X-ray diagrams of castables matrices after drying (110 °C) and firing at temperatures of 800 °C, 1000 °C, and 1200 °C: MCA-0,8 (a), and MCA-1,3 (b)

According to XRD and petrographic researches the castables samples after thermal treatment on air and in the carbon-containing atmosphere consist mainly of anorthite and calcium dialuminate. The optical microscopy reveals that all samples have the aggregate grains which consist of anorthite (initial) and binding mass (matrix) which consists of high alumina cement mineral remnants, perlite, alumina silicate, cryptocrystalline matter and anorthite (secondary) arising due to the interaction between the cement and additives in the matrix of the castable. For confirmation of this assumption researches, which results are explained below, were carried out.

The research of phase's formation in the castables matrix was carried out when heating up to temperature 1200 °C. Samples for the research were prepared taking into account a ratio of components in a matrix (high-alumina cement, perlite, FGNAS) of the castables, namely – for CA-0,8 castable matrix a ratio high-alumina cement : perlite – 4 : 1, and for CA-1,3 castable matrix a ratio high-alumina cement : FGNAS : perlite – 8 : 3 : 1.

X-ray diagrams of the castables matrixes samples before and after firing are given in Fig. 3.

In the cement and perlite mix (MCA-0,8) the main crystal phase is CA_2 (Fig. 3 a) since the perlite represents volcanic glass which for an X-ray radiation is amorphous. Traces of other phases in an initial state and after firing at temperatures of 800 °C are not fixed. After firing at a temperature of 1000 °C on the X-ray diagram there are anorthite traces that testify to the beginning of interaction between perlite and cement.

Fig. 3 b shows that, in the mix of high-alumina cement, FGNAS and perlite (MCA-1,3) the main crystal phases are CA_2, kyanite and sillimanite. Traces of other phases in an initial state and after firing at temperatures of 800 °C are not fixed. After firing at a temperature of 1000 °C on the X-ray diagram weak traces of the anorthite are visible. After firing at a temperature of 1200 °C on the X-ray diagram legible diffraction lines of the anorthite appear.

The anorthite content defined by the XRD analysis is given in Tab. 10.

Thus, by results of the phase formation researches at thermal treatment of the heat insulating castable matrixes, it is estab-

lished that, in the MCA-0,8 and MCA-1,3 samples the anorthite formation happens already at 1000 °C, however, it goes in the MCA-1,3 sample more intensively. This explains the castable stability in the carbon-containing atmosphere as a result of binding of the matrix components in steady against reducer secondary anorthite, as well as decrease of linear dimensions change in the service due to shrinkage compensation at sintering as a result of the anorthite formation with volume increase.

Tab. 10 **The anorthite content [%] in MCA-0,8 and MCA-1,3 samples depending on firing temperature**

Composition	Firing Temperature [°C]	
	1000	1200
MCA-0,8	9	13
MCA-1,3	20	24

5 Conclusions

The manufacturing technology of anorthite aggregate with a microporous structure is developed. Unlike traditional production in the developed technology, the burning-out additives and foam are not used, and a foam agent is water withheld in green structure and providing micropores formation at stages of drying and firing of products owing to what the received aggregate has the low thermal conductivity coming to thermal conductivity of ceramic fibre products.

On the basis of anorthite microporous aggregate, the heat insulating castables of two compositions with an apparent density of 0,8 g/cm^3 and 1,3 g/cm^3 are developed, the possibility of their use in carbon-containing atmospheres at temperatures up to 1200 °C is shown. Phase formation in the castable matrixes is studied, as well as formation of secondary anorthite in the matrix is established that promotes resistance of the castable to carbon-containing atmosphere influence.

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