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A PHYSICOCHEMICAL STUDY OF PROPERTIES OF INTEGRATED HIGH-TEMPERATURE HEAT-INSULATING MATERIALS

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Results of a study of properties of integrated high-temperature heat-insulating materials based on expanded vermiculite are reported. These materials combining low heat conductivity and high strength, have a potential for use as lining refractories in thermal power units with operating temperatures not exceeding 1100°C.

Introduction of a porous filler into a material is a method widely used in industry for achieving a porous structure in the material. The expanded vermiculite exhibits a range of unique properties such as a low bulk density (80 – 120 kg/m^3), low heat conductivity (0.04 – 0.12 W/(m · K)), and relatively high melting point (1240 – 1430°C); furthermore, it is chemically inert, durable, and environmentally safe [1]. All these properties show that the expanded vermiculite can be a promising candidate for use as the porous filler for fabrication of high-temperature heat-insulating materials.

Heat-insulating vermiculite-based products are composed of an expanded vermiculite (porous filler), a refractory clay, possibly containing additives (the bond), and a nonplastic refractory material — chamotte, dust collected in electric filters (refractory filler). At the Borovichi Refractory Kombinat (BRK) JSC, the so-called integrated high-temperature heat-insulating materials (ITOM-grade) based on the above vermiculite-based formulation have been developed [2, 3]. Each of the ITOM ingredients was selected for a specialized function: disperse refractory fillers jointly with a plastic mineral binder (refractory clay, kaolin) form, when calcined, a refractory matrix, which improves the mechanical strength and refractoriness of the product; the expanded vermiculite allows achievement of superior heat-insulating properties and thermal stability.

To study processes involved in the sintering of ITOM green preforms, compositions were selected that included a refractory clay with additives, expanded vermiculite, and refractory fillers (electric filter dust and chamotte) taken in varying proportions. The characteristics of precursor materials and finished products are given in Table 1.[2] The test specimens were prepared by a method in [3]. The dried (not calcined!) specimens were ground in a porcelain mortar and pestle and analyzed on a Mettler Toledo derivatograph.[3] Typical ITOM derivatogram (composition *2*) is shown in Fig. 1.

The physicochemical processes involved in the ITOM heat treatment can be formulated in the following way:

– removal of physical moisture in the temperature range of 60 – 160°C (an endo-effect peak for different compositions was recorded at 114 – 134°C);

– removal of the loosely held chemically bound water in the hydrous layers sandwiched between micaceous vermiculite packets, in the range 160 – 290°C (an endo-effect peak at 218 – 265°C);

– removal of the crystallohydrate water from the hydrous vermiculite layer at 260 – 480°C co-current with the burnout of organic plasticizer CMC (carboxymethyl cellulose), with an exo-thermal effect markedly superior to the endo-thermal effect of vermiculite dehydration (exo-effect peak at 297 – 373°C);

– decomposition of kaolinite in the range of 315 – 825°C (endo-effect peak at 526 – 537°C);

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[3] Differential thermal analysis was carried out by S. D. Stepanova, Physical Chemistry Department, CITP.

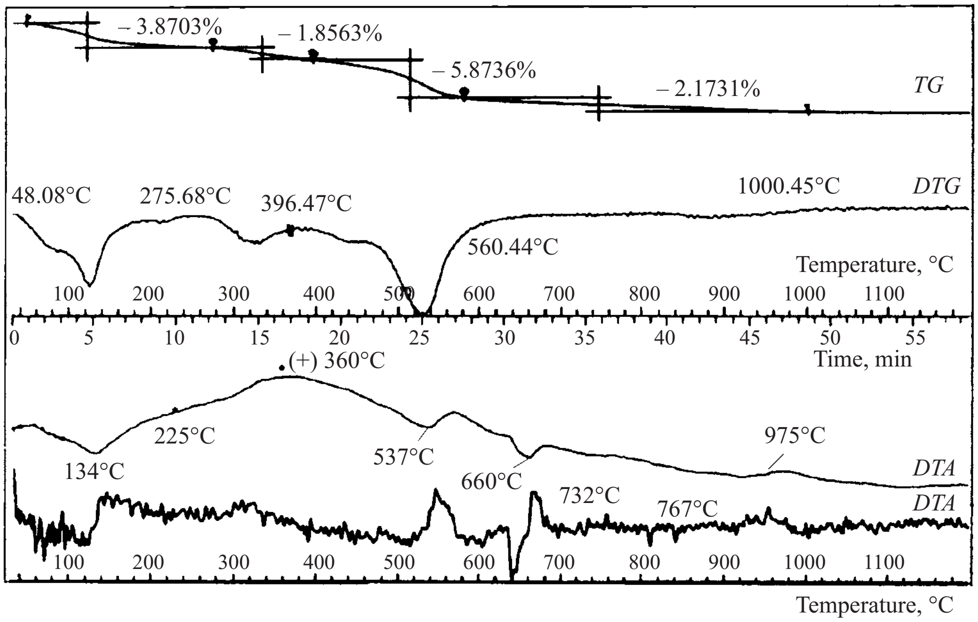

Fig. 1. Derivatograms of the specimens of composition *2*.

– removal of the crystallohydrate water of micaceous vermiculite packets (9.07% mass loss) at temperatures above 480°C (endo-effect peak at 660 – 743°C);

– crystallization of the amorphous products of kaolinite decomposition to yield a metastable alumosilica spinel or γ-Al_2O_3 in the range of 950 – 1050°C with a maximum at 975 – 988°C (the so-called kaolinitic effect).

To study the ITOM high-temperature processes, typical compositions with the apparent density ranging from 400 to 1000 kg/m^3 were selected. The specimens were prepared by a method in [3]; they were calcined at 1000°C for 1 h using a Snol electric furnace. The once calcined specimens were subjected to repeated calcination at 1100, 1200, and 1300°C.

A state diagram for the $MgO – Al_2O_3 – SiO_2$ system in which compositions under study were indicated using appropriate conversion factors [4] is shown in Fig. 2. Point *1* (composition *1*) belongs to the elementary triangle enstatite – cordierite – silica; it is located in the crystallization field of cordierite. Under equilibrium conditions, the occurrence of a liquid phase during heating is controlled by the invariant point *A* at 1355°C. Point *2* (composition *2*) belongs to the elementary triangle mullite – cordierite – silica; it is located in the crystallization field of mullite and virtually coincides with the cordierite point $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$. The incongruent melting point for cordierite is 1465°C. The melting point of a ternary eutectic is 1440°C (point *B*). Point *3* (composition *3*), like point *2*, belongs to the elementary triangle mullite-cordierite-silica and is located in the crystallization field of mullite. Under equilibrium conditions, the occurrence of a liquid phase on heating is controlled by invariant point *B* at 1460°C. With fluxes added (Na_2O, K_2O, CaO, Fe_2O_3, and TiO_2), the melting point will tend to decrease.

TABLE 1. Chemical Composition of the Percursor Ingredients and Heat-Insulating Products

Material	Chemical composition, wt.%						
	Al_2O_3	Fe_2O_3	SiO_2	CaO	MgO	TiO_2	$Na_2O + K_2O$
Ingredient:							
expanded vermiculite	15.54	3.21	43.53	5.29	30.33	1.37	0.74
KBLP-2-grade kaolin	34.89	2.19	57.34	0.8	0.7	2.16	1.92
electric filter dust	43.8	2.36	49.9	0.9	0.72	1.9	0.42
chamotte	40.84	2.98	51.9	0.99	0.7	2.2	0.39
Product (composition):							
1	23.3	2.8	49.1	3.5	18.5	1.7	1.2
2	31.8	2.5	51.0	2.2	9.6	1.8	1.1
3	33.7	2.4	52.3	1.7	6.6	1.9	1.2

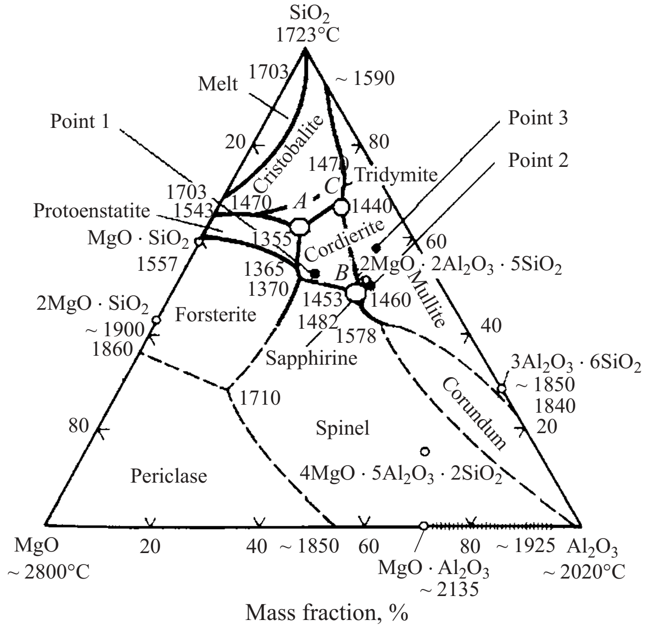

Fig. 2. State diagram of the $MgO – Al_2O_3 – SiO_2$ system with compositions under study indicated.

It is seen in the state diagram that cordierite $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ is the first crystalline phase that makes its appearance at a temperature close to eutectic. After MgO becomes completely bound into cordierite, the remaining oxides of aluminum and silicon combine to form mullite. The higher the melting point, the higher the refractory properties of a material; in the compositions of interest, the trend is *1* (1355°C) → *2* (1440°C) → *3* (1455°C).

The phase composition of heat-insulating vermiculite materials treated at high temperatures was studied by x-ray phase analysis. The sintered specimens of each composition following the primary and secondary calcination were examined using a DRON-6 x-ray diffractometer.[4] Diffraction patterns for compositions *1* – *3* following the primary calcination at 1000°C and secondary calcination at 1100, 1200, and 1300°C are shown in Fig. 3.

Expanded vermiculite sintered at 850 – 950°C undergoes decomposition to yield clinoenstatite; in this process, the particles retain their size, and clinoenstatite forms a pseudomorph after vermiculite. In the diffraction patterns of all specimens sintered at 1000°C, we observed reflections due to clinoenstatite (0.316, 0.287, 0.246, 0.221, and 0.152 nm) and kaolinite decomposition products: quartz (0.287, 0.246, and 0.139 nm), or cristobalite and γ-Al_2O_3 (0.425, 0.334, and 0.246 nm) and the crystalline phase of the refractory filler mullite (0.539, 0.339, 0.252, and 0.270 nm). Thus, in the products sintered at 1000°C, the vermiculite filler achieves complete mineralization, whereas in the kaolin bond the process stops at an intermediate stage — crystallization of the primary decomposition products of kaolinite; however, formation of mullite from the electric filter dust fails to come to an end.

Heating to higher temperatures results in the occurrence of a liquid phase and sintering: the material improves in strength and shows shrinkage and loss of heat-insulating properties. Calcination of specimens *1* at 1100°C results in the formation of cordierite (reflections 0.850, 0.316, and 0.245 nm). The slight shift of cordierite lines towards the smaller angles possibly occurs because of the isomorphic replacement of magnesium oxide by iron (II) oxide. In specimens of other compositions, no presence of cordierite was detected.

In all specimens calcined at 1200°C, a decrease in clinoenstatite line intensity and an increase in cordierite line intensity was observed. This effect may be due to a process by which enstatite is spent on the formation of cordierite. Noteworthy is that the formation of cordierite in all specimens, irrespective of the kind of refractory filler used, takes place within the same temperature range from 1100 to 1200°C.

Specimens of composition *1* calcined at 1300°C displayed partial melting. Their x-ray diffraction patterns showed the presence of clinoenstatite and cordierite, also mullite in smaller amounts. In specimens of composition *2* and *3* calcined at 1300°C, mullite and cordierite phases were identified. The shift of cordierite lines towards the larger angles may be explained by the formation of a solid solution of ferrocordierite produced by partial isomorphic substitution of Mg^{2+} ions by Fe^{2+}.

The precursor ingredients react chemically to yield cordierite and mullite. In ITOM compositions high in vermiculite and free of refractory filler, the formation of cordierite starts at 1100°C; in compositions containing a refractory filler, the process starts at temperatures higher than 1200°C. The compositional increase in expanded vermiculite causes a decrease in melting temperature accompanied by a degradation of high-temperature strength and the occurrence of shrinkage. An increase in refractory binder and filler produces an exactly opposite effect.

Reliability, durability, and service efficiency of thermal power units are controlled by physicomechanical and high-temperature properties of the heat-insulating materials used. To test ITOM properties, specimens of different apparent density were prepared. As an example, typical products are shown in Fig. 4; relevant results are given in Table 2.

In dried and calcined ITOM specimens, the shrinkage is uniform in all directions, which makes it possible to obtain net shape components, even of large size, without further mechanical finish (see Fig. 4). The air shrinkage increases from 1.2 to 3.5% as the clay component percentage increases from 40 to 50%. The fire shrinkage in specimens with different apparent density falls into a rather narrow range of 1.8 – 2.3%.

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[4] X-ray phase analysis was carried out by S. D. Stepanova, Physical Chemistry Department, CITP.

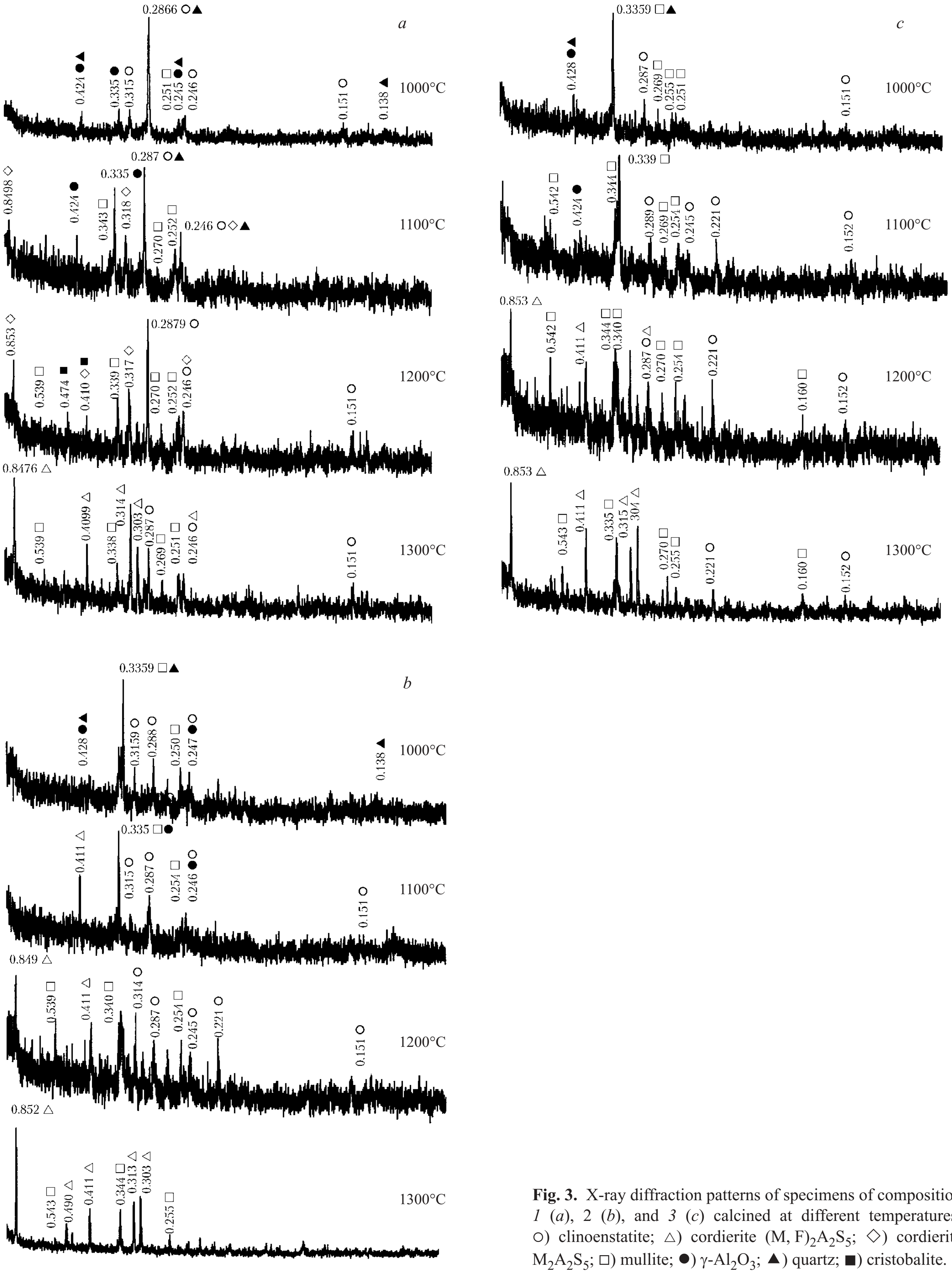

Fig. 3. X-ray diffraction patterns of specimens of composition *1* (*a*), 2 (*b*), and *3* (*c*) calcined at different temperatures: ○) clinoenstatite; △) cordierite $(M, F)_2A_2S_5$; ◇) cordierite $M_2A_2S_5$; □) mullite; ●) γ-Al_2O_3; ▲) quartz; ■) cristobalite.

Fig. 4. The appearance of integrated high-temperature heat-insulating materials.

The vermiculite heat-insulating components with low apparent density ($\rho_{ap} = 400 – 1000\ \text{kg/m}^3$) show a compressive strength rather high for heat insulators, $\sigma_c = 0.9 – 2.4$ MPa, which is a convenience for their transportation, mounting, and service in thermal power units. ITOM components, when compared to the conventional heat insulators, feature more advantageous characteristics: for the apparent density of 400 – 1000 kg/m^3, the heat conductivity at 200°C lies within 0.09 – 0.23 W/(m · K). For comparison, the heat conductivity of fibrous heat-insulating materials is 0.12 – 0.15 W/(m · K), for diatomite components, it is 0.2 – 0.3 W/(m · K), and for ultra-lightweight chamotte components — 0.18 – 0.22 W/(m · K) (at $\rho_{ap} = 400\ \text{kg/m}^3$).

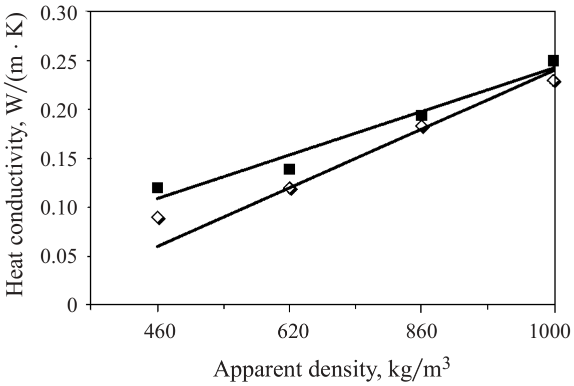

Fig. 5. Heat conductivity plotted as a function of the ITOM apparent density: *1*) average temperature 200°C; *2*) 380°C.

Heat conductivity λ as a function of the apparent density ρ_{ap} can be expressed in the following way (Fig. 5):

at an average temperature of 200°C:

$$\lambda(\rho) = \lambda_{400} + 0.000292\rho,$$

at an average temperature of 380°C:

$$\lambda(\rho) = \lambda_{400} + 0.000217\rho,$$

where $\lambda(\rho)$ is the heat conductivity of components with apparent density ρ, kg/m^3; λ_{400} is the heat conductivity of components with apparent density 400 kg/m^3.

TABLE 2. Specifications of Newly Developed Heat-Insulating Components*

Property	Component grade				Standard for measuring method or instrument
	ITOM-440	ITOM-620	ITOM-860	ITOM-1000	
Apparent density, kg/m^3	420 – 500	600 – 640	850 – 900	1000 – 1100	GOST 24468–80
Compressive strength, MPa	0.9 – 1.0	1.0 – 1.4	1.4 – 1.7	2.0 – 2.4	GOST 4070.2–97
Open porosity, %	80 – 82	75 – 78	65 – 68	62 – 65	GOST 2409–95
Shrinkage, %:					
1150°C, 2 h	1.4 – 1.5	1.2 – 1.4	1.1 – 1.3	1.0 – 1.2	GOST 5402.2–2000
900°C, 8 h	0.2	No data available			
Incipient material softening, °C, under load, MPa:					
0.05	1109	1119	1135	1140	GOST 4070–2000
0.04	1120	–	–	–	
0.06	–	1118	–	–	
0.08	–	–	1117	–	
0.1	–	–	–	1108	
Heat conductivity, W/(m · K), at average temperature, °C:					
200	0.090	0.120	0.183	0.230	GOST 12170–85
380	0.120	0.139	0.194	0.250	

* For all materials, the test for thermal stability was more than 100 heat-and cool cycles 1000°C – air (GOST 4071.2–94).

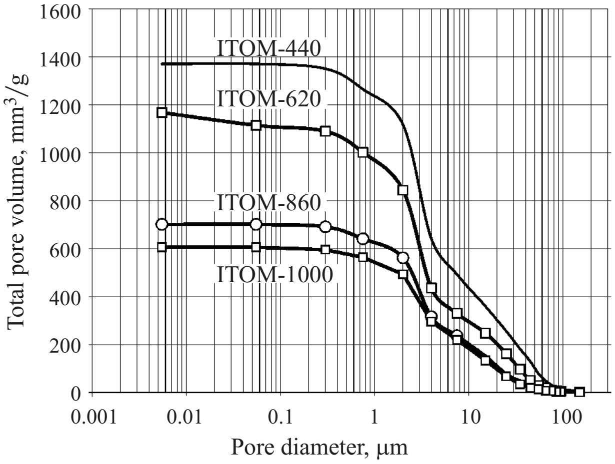

Fig. 6. Pore size distribution in ITOM specimens of different apparent density.

With increase in temperature, the effect of open porosity on ITOM heat conductivity tends to decrease owing to the increasing role of the radiation component in the heat-transfer process. A relationship of this kind is typical of most porous bodies.

The refractory kaolin-based matrix in ITOM products provides volumetric constancy in subsequent heatings and high incipient softening temperature. These properties control the limiting service temperature of heat-insulating materials at high temperatures.

Temperature for the onset of material softening according to the State Standard GOST 4070–2000 is determined under a load of 0.2 MPa. Such a load may arise in the footing course of thermal power units made from dense refractory materials (with a density over 2.0 g/cm^3). However, the load in the footing course of heat insulation is much smaller because of the low density. In conformance with the ISO 1893–89 International Standard, a load of 0.05 MPa has been recommended for determining the temperature of onset of softening in lightweight heat insulating materials. According to current recommendations, the load in the study of heat-insulating materials should be selected with allowance for the average apparent density of the material (for example, for the apparent density of 400 kg/m^3, the load should be 0.04 MPa, and for 300 kg/m^3 — 0.03 MPa) [5]. Therefore the incipient softening temperature was determined in duplicate measurement: under a load of 0.05 MPa and under a load depending on the average apparent density. The two temperatures for the onset of softening in components of different density were within the limits of 1108 – 1140°C and differed within the accuracy of the measuring method used.

The linear aftershrinkage produced by the second firing at 1150°C for 2 h may serve as a measure of the high-temperature volumetric constancy. In the newly developed materials, the aftershrinkage does not exceed 1.5%. According to GOST 5040–96, the limiting aftershrinkage should not exceed 1.0%; still, with allowance for the specific service conditions of heat-insulating materials, the results for volumetric constancy of ITOM components may be accepted as quite satisfactory.

Thus, based on the test results for incipient softening and aftershrinkage, the temperature of 1100°C may be taken as limiting for the use of the newly developed integrated high-temperature heat-insulating materials.

The high porosity of heat-insulating materials is responsible for their major thermophysical and mechanical properties such as apparent density, heat conductivity, and strength. Therefore the ITOM materials were tested for porosity characteristics[5] by the mercury porosimetry using Pascal-140 and Pascal-240 high-pressure porosimeters operating at a maximum pressure of 400 MPa (Fig. 6).

With increasing apparent density of the material from 440 to 1000 kg/m^3, the pore volume decreases by a factor of 2.2 — from 1370 to 606 mm^3/g (see Fig. 6). The pore size distribution did not show significant change. Predominant are pores from 0.5 to 10 μm across; they account for 65 to 70% of the total pore volume. The volume due to micropores (less than 0.1 μm across) and macropores (more than 100 μm across) is insignificant.

The fine porous structure of ITOM specimens provides high strength and high insulating properties at high temperatures despite their low apparent density. The thermal stability was measured using test specimens shaped as cubes with an edge of 50 mm. The standard procedure according to GOST 4071.2–94 requires the use of running water to cool specimens heated 1000°C; however, it is little suited for ITOM specimens because of the high water uptake. For this reason, the specimens removed from a furnace were cooled in air. All the materials irrespective of their composition displayed high thermal stability. Subjected to a total of 100 heat-and-cool cycles 1000°C – air, the specimens sustained no damage, except for occasional cracking.

CONCLUSIONS

The ITOM composition controls the high-temperature properties: the increased content of expanded vermiculite causes a decrease in melting point and high-temperature strength and an increase in shrinkage, whereas the increased content of refractory bond and filler produces exactly opposite effects.

The ITOM products, for all their low apparent density, exhibit a high strength and a low linear aftershrinkage at 1150°C (not exceeding 1.5%). The thermal strain under load and aftershrinkage change but slightly with increasing apparent density of the material.

The high-temperature heat-insulating vermiculite materials, owing to their fine porous structure with the predominance of pores 0.5 – 10.0 μm across, exhibit superior heat-insulating ability and thermal stability.

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[5] Mercury porosimetry measurement were carried out by A. V. Efimov, Physical Chemistry Department, CITP.

The integrated heat-insulating high-temperature materials can be safely employed at temperatures not exceeding 1100°C.

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