THERMAL CONDUCTIVITY OF REFRACTORY FILLS AT TEMPERATURES IN THE RANGE 500-2000 K

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Experimental data on the thermal conductivity of refractory fills based on MgO, Y_2O_3, ZrO_2, and Al_2O_3 with different fraction composition were obtained. The limits of applicability of the model of thermal conductivity of granular systems for materials of this class were determined.

Refractory fills are promising materials for high-temperature thermal insulation. Analysis of the published works, however, shows that their thermal conductivity has not been adequately studied [1, 2]. The existing published data have a large spread (50-100% and larger) and cover a comparatively narrow temperature range from 400 to 1500 K, which is much lower than the real temperature at which the fills are employed. This is apparently attributable to the difficulties in performing high-temperature measurements as well as the fact that the description of the structure of granular materials is not unique. The experimental study of the effect of different factors on the thermal con ductivity of refractory fills is a very difficult and laborious problem. It is thus especially important to develop a mathematical model relating the composition and structure of granular materials with the effective thermal conductivity. The model of the granular material presented in [3, 4], in our opinion, best describes a real refractory fill, since it includes the structure of the fills, the parameters of the contact of the particles, the shape of the gap between the particles, etc. All parameters in the working formulas have a definite physical meaning and can be determined independently, which makes the model very convenient for analyzing the effect of different factors on the thermal conductivity.

The purpose of this work is to check this model experimentally at temperatures in the range 500-2000 K and to predict based on it the thermal conductivity of some fills that have not yet been studied experimentally.

The thermal diffusivity was measured directly in the experiment using the method of [5]. The measurements were performed by the method of monotonic heating of cylindrical samples. The limit of the total (systematic plus random) error in the measurements equals 10-13%, depending on the temperature and the thermocouples employed, with a confidence probability of p = 0.9. Then the thermal diffusivity was converted into thermal conductivity based on the known values of the bulk mass and the heat capacity [1]. The samples studied are briefly described in Table 1. The average grain size in the range 10^{-3} mm up to 10 mm was studied by different methods: by sieve analysis for fractions larger than 0.06 mm and by the sedimentation method on the Sedigraf 5000D apparatus for smaller fractions. The porosity of the grains was measured using the procedure of GOST 18847-84 as well as the method of mercury porometry using high- and low-pressure mercury porometers.* In addition, Table 1 gives the coefficients of the smoothed temperature dependences of the thermal conductivity in the range 473-2073 K for the first high-temperature heating (above 1500 K) and subsequent repeated heatings in the same temperature range in nitrogen at normal pressure ($\approx 10^5$ Pa), as well as the statistical characteristics of the curves — rms deviation σ and the correlation coefficient k.†

* The measurements of the structural characteristics of the samples were performed under the direction of Candidate of Chemical Sciences F. S. Kaplan.
† The statistical analysis of the measurements was performed by M. F. Gurari on a computer.

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TABLE 1. Properties of the Fills Studied

Grain material	Fraction, mm	Av. grain size, mm	Bulk mass $\rho_b \cdot 10$, kg/m³	Grain porosity	First heating: $\lambda=a+bt+ct^2$, W/(m·K)			σ, W/(m·K)	k	Repeated heating: $\lambda=a+bt+ct^2+dt^3$, W/(m·K)				σ, W/(m·K)	k
					a	$b \cdot 10^3$	$c \cdot 10^6$			a	$b \cdot 10^3$	$c \cdot 10^6$	$d \cdot 10^9$		
Magnesite MgO	5,0—2,5	3,710	1,52	0,16	0,439	—	0,630	0,013	0,977	0,436	—	0,780	—	0,037	0,997
Same	2,5—1,0	1,675	1,56	0,17	0,391	—	0,574	0,109	0,904	0,539	—	0,406	0,132	0,052	0,997
»	1,0—0,5	0,737	1,62	0,16	0,395	—	0,471	0,048	0,994	0,583	—0,142	0,486	—	0,039	0,996
»	<0,5	0,265	1,78	~0,05	0,234	0,160	—	0,050	0,987						
					0,379*)	—	0,370	0,132	0,850	1,947	—0,512	—	—	0,169	0,836
Fused yttrium oxide PIT-1	⩽1,0	0,633	2,61	~0	0,366	0,482	—	0,034	0,987	0,705	—0,616	0,130	—0,497	0,020	0,991
Single-crystalline corundum MK-16	0,27	0,270	2,10	~0	0,339	—	0,399	0,074	0,985	1,029	—0,742	0,611	—0,756	0,019	0,993
Single-crystalline corundum MK-25	0,37	0,370	2,07	~0	0,322	0,175	0,242	0,022	0,998	0,606	0,244	0,174	—	0,019	0,998
Single-crystalline corundum MK-40	0,65	0,650	2,05	~0	0,333	0,193	0,241	0,021	0,988	0,648	—	0,212	—	0,027	0,993
Zirconium dioxide PTsT-90	8—10	7,4	2,84	0,27	0,044 †	1,240	—	0,153	0,975	—	—	—	—	—	—

* The polynomial λ(t) is used in the range 473-1173 K.
† The polynomial λ(t) is used in the range 473-1473 K.

TABLE 2. Physical Characteristics of the Particles (Grains) of the Fills Studied [1, 6]

Fill	Fraction mm	Apparent grain density $\rho_s \cdot 10^3$, kg/m³	Thermal conductivity λ_s, W/(M·K) at the temperature, K					Emissivity ε at the temperature, K				
			473	873	1273	1673	2073	473	873	1273	1673	2073
Magnesite	5,0—2,5	2,95	11,24	7,07	4,69	4,10	5,29	0,68	0,49	0,35	0,31	0,31
Same	2,5—1,0	2,98	11,24	7,07	4,69	4,10	5,29	0,68	0,49	0,35	0,31	0,31
Same	1,0—0,5	2,92	9,79	6,23	4,07	3,30	3,94	0,68	0,49	0,35	0,31	0,31
Same	<0,5	3,20	13,24	8,32	5,50	4,80	6,20	0,68	0,49	0,35	0,31	0,31
Yttrium oxide PIT-1	⩽1*)	4,84	14,50	7,80	5,70	5,10	4,05	0,5	0,5	0,5	0,5	0,5
Single-crystalline corundum MK-16 MK-25, MK-40		3,87	22,89	9,76	6,04	5,48	5,90	0,74	0,61	0,47	0,34	0,37
Zirconium dioxide PTsT-90	8—10	4,40	1,05	1,09	1,19	1,36	1,58	0,73	0,49	0,38	0,41	0,45

* The data for the emissivity were selected based on general physical considerations.

TABLE 3. Size Distribution of the Particles in a Magnesite Fill with a Fraction < 0.5 mm

Fraction limits, μm	500—160	400—160	160—63	63—36	36—25	25—16	16—10	10—6,3	6,3—4,0	4,0—2,5	2,5—1,6	1,6—1,0	$\overline{V}$
Percentage content mass %	29,9	44,1	1,3	3,1	6,8	7,8	3,8	0,6	0,4	0,4	0,1	0,2	1,5

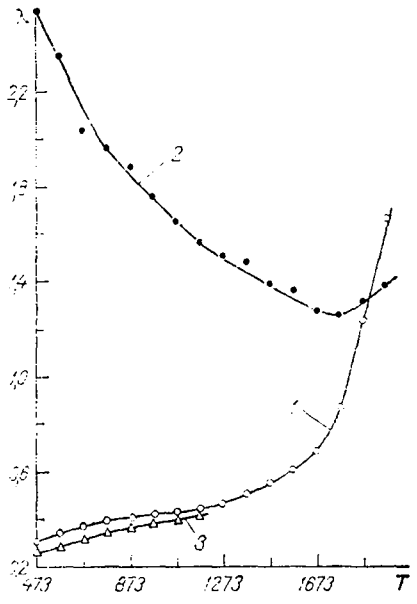

Fig. 1

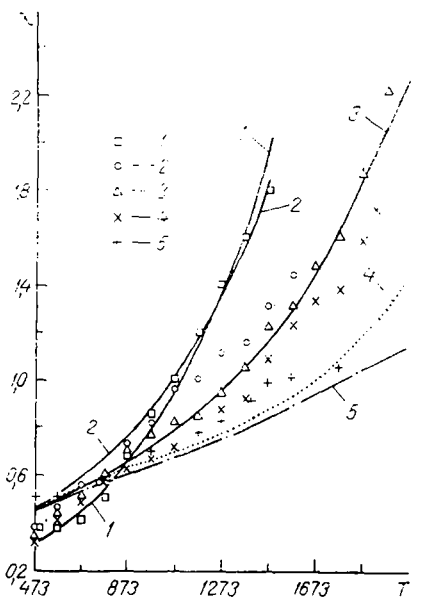

Fig. 2

Fig. 1. Thermal conductivity of magnesia fill with grain size d < 0.5 mm: 1) first heating; 2) repeated heatings; 3) repeated low-temperature heatings (the difference between the curves 1 and 3 is explained by the difference in the bulk masses of the fills: ρ_{b_1} = $1.78 \cdot 10^3$ kg/m^3, ρ_{b_3} = $1.61 \cdot 10^3$ (kg/m^3)·W/(m·K), T, K.

Fig. 2. Thermal conductivity of different fills: the curves were calculated by the model of [3, 4]; the dots are the experimental points; 1) PTsT-90 zirconium dioxide, fraction $\leq$ 10 mm; 2) magnesite, fraction 5.0-2.5 mm; 3) magnesite, fraction 2.5-1.0 mm; 4) magnesite, fraction 1.0-0.5 mm; 5) PIT-1 yttrium oxide, fraction $\leq$ 1.0 mm.

Analysis of the results shows that the thermal conductivity of fills with grain sizes exceeding 0.5 mm under repeated heatings (10-15 heatings up to maximum temperatures were performed) is somewhat higher (by 10-15%) than the initial values. This is apparently explained by the sintering of the particles with high-temperature heatings. At the same time, with repeated heatings up to 1200-1500 K (low-temperature heatings), when sintering does not occur, the data are practically reproduced. For fine-grained fills with particle sizes less than 0.5 mm the sintering effect following high-temperature heating of the samples becomes dominant (Fig. 1) and qualitatively changes the character of the dependence — instead of the increase in the thermal conductivity with increasing temperature, characteristic for fills, a drop in the thermal conductivity following Éiken's law [1], typical for dense magnesite refractory materials, is observed.

Examination of the structure of freely poured refractory fills under a binocular microscope and based on the bulk mass showed that such granular materials do not have a three-dimensional network of voids, i.e., they are formed only by a first-order structure — a "framework," whose porosity falls in the range 0.26-0.40.

The working relations of the model of [3, 4] for such a structure have the following form:

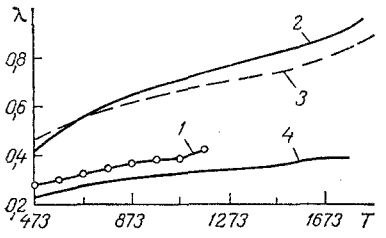

Fig. 3

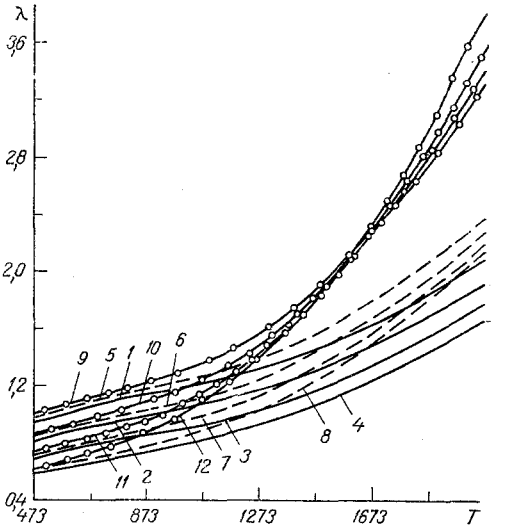

Fig. 4

Fig. 3. Thermal conductivity of magnesite fill with grain size d < 0.5 mm: 1) experimental data for low-temperature heatings; 2) calculation based on the model of a monodispersed fill [3, 4]; 3, 4) calculation based on the model of a polydispersed fill [10]; 3) two-component mixture, $d_1 = 23.5 \cdot 10^{-6}$ m, $m_1 = 24.7\%$, $d_2 = 298 \cdot 10^{-6}$ m, $m_2 = 75.3\%$; 4) three-component mixture $d_1 = 0.5 \cdot 10^{-6}$ m, $m_1 = 1.5\%$, $d_2 = 24.95 \cdot 10^{-6}$ m, $m_2 = 23.2\%$, $d_3 = 298 \cdot 10^{-6}$ m, $m_3 = 75.3\%$ (d_i is the average particle size of the i-th fraction, m_i is the mass fraction of particles in the i-th fraction in the mixture $\sum_{i=1}^{3} m_i = 1$).

Fig. 4. thermal conductivity of corundum fills with different fractions: 1-4) 0.5-1.0 mm fraction; 5-8) 1.0-2.5 mm fraction; 9-12) 2.5-5.0 fraction; bulk masses: 1, 5, 9) $\rho_b = 2.66 \cdot 10^3$ kg/m^3; 2, 6, 10) $\rho_b = 2.52 \cdot 10^3$ kg/m^3; 3, 7, 11) $\rho_b = 2.34 \times 10^3$ kg/m^3; 4, 8, 12) $\rho_b = 2.16 \cdot 10^3$ kg/m^3; the apparent density of the particles of the fill $\rho_s = 3.6 \cdot 10^3$ kg/m^3.

$$\lambda_{eff} = \frac{\lambda_s}{y_4^2}\left\{\frac{y_1}{0{,}5\bar{h}_{irr} + (1 - 0{,}5\bar{h}_{irr})\Phi} + \left\{\frac{D}{y_3^2} + \right.\right.$$

$$+ \left[\frac{A}{1 - 0{,}5\bar{h}_{irr} - B + 0{,}5\bar{h}_{irr}\nu_{f.f.}} + \frac{2\nu_g}{1 - \nu_g} \times \right.$$

$$\left.\left.\left. \times \left(D - F + w \ln \frac{w - D}{w - F}\right)\right]^{-1}\right\}^{-1}\Bigg\};$$

$$A = y_2^2 - y_1^2; \quad F = \sqrt{1 - y_2^2}; \quad D = \sqrt{1 - y_3^2}; \quad E = y_4^2 - y_3^2;$$

$$w = [1 - \nu_{a.f}\sqrt{1 - y_3^2} + B/pd](1 - \nu_{a.f})^{-1}; \quad d = 2r;$$

$$\nu_{a.f} = \frac{\lambda_{a.f}}{\lambda_s}, \quad \nu_{a.f} = \frac{\lambda_{a.f}}{\lambda_s}, \quad \nu_g = \frac{\lambda_g}{\lambda_s}; \quad \bar{h}_{irr} = \frac{h_{irr}}{r};$$

$$B = \frac{4c_p/c_V}{1 + c_p c_V}\,\frac{2 - a}{a}\,\Lambda_0 P_0 \,\mathrm{Pr}^{-1};$$

$$y_1 = (3{,}3 \cdot 10^{-3} \div 10^{-1})\, y_2;$$

$$y_2 = 3{,}3 \cdot 10^{-3}\sqrt[3]{(1 - m_2)^{-2/3}\,[p_{sp} + 10\rho_s\,(1 - m_2)h_\ell}\,;$$

$$y_3 = \frac{r_3}{r} = \frac{2\sqrt{N_c - 1}}{N_c}; \quad y_4 = \frac{r_4}{r} = \frac{y_3}{\sqrt[3]{1 - m_2}};$$

$$m_2 = 1 - \frac{\rho_b}{\rho_s}; \quad N_c = \frac{m_2 + 3 + \sqrt{m_2^2 - 10m_2 + 9}}{2m_2};$$

$$\Phi = 0{,}017 + 0{,}4y_1;$$

$$\lambda_{f.f.} = \lambda_{f.f.m.} + \lambda_{f.f.\ell.} = \lambda_g[1 + B/(ph_{irr})]^{-1} + \varepsilon_{lim}\sigma_{S\text{-}B}h_{irr}T^3;$$

$$\lambda_{a.f.} = \lambda_{a.f.m.} + \lambda_{f.f.\ell.} = \lambda_g[1 + B/(p\delta_{a.f.})]^{-1} + 4\varepsilon_{lim}\sigma_{S\text{-}B}\delta_{a.f.}T^3;$$

$$\varepsilon_{lim} = \frac{\varepsilon}{2 - \varepsilon}; \quad \delta_{a.f.} = d(\bar{h}_{irr} + N_c^{-1}).$$

Figure 2 compares the computed and experimental values of the thermal conductivity of refractory fills, whose properties are given in Table 1. The data were compared in a medium of nitrogen at a pressure of 10^5 Pa. The thermal conductivity and density of the fill particles studied, necessary for the calculation, are given in [1], the emissivity of the particles is given in [6] (see Table 2), and the properties of the gas (Λ_0; c_p/c_V; Pr; λ_g) are given in [7-9]. For nitrogen $\Lambda_0 = 6.28 \cdot 10^{-8}$ m, Pr = 0.698, $c_p/c_V = 1.4$ [7, 8].

As one can see from the figure, the computational results agree well with experiment in a wide range of temperatures for monofractional fills with grain sizes of 10-0.5 mm; for zirconium dioxide fill with grain sizes of 10-8 mm and magnesia fill with grain sizes of 5.0-2.5 mm the rms deviation of the experimental results from the computed curve equals σ_1 = 7.5 and 15.4%, respectively, in the temperature range 300-1500 K; for magnesite fills with the fractions 2.5-1.0 and 1.0-0.5 mm σ_1 equals 12.3 and 18.8%, respectively, in the temperature range 500-2100 K. The greatest discrepancy is observed for magnesite fill with the fraction 1.0-0.5 mm at high temperatures: $|(\lambda^{calc} - \lambda^{exp}):\lambda^{exp}| = 24\%$. At the same time for a fill consisting of fused yttrium oxide with an analogous fraction composition good agreement was obtained between calculation and experiment: $\sigma_1 = 10.2\%$ in the entire temperature range.

Granulometric studies, performed by the sieve method and by means of sedimentation measurements, showed that the grain composition of finely dispersed magnesite fill with a fraction < 0.5 mm exhibits a significant spread: from 500 μm up to several μm (Table 3).

Figure 3 shows the experimental and computed data for the thermal conductivity of this multicomponent, finely dispersed fill. Comparison of the computed curves 2, 3 and the experimental curve 4 shows that when the effective thermal conductivity of the particles of the fine fraction (< 1 μm), whose mass fraction is very small (m = 1.5%) is neglected a significant disagreement is observed between these curves. Curve 4 was calculated using the model of thermal conductivity of a polydispersed fill (three particle sizes) [10], in which the fine fraction itself had the following characteristics: $d_3 = 0.5 \cdot 10^{-6}$ m and $m_3 = 1.5\%$. In addition, the technique, described in [3], for reducing a multicomponent structure to a two-component structure was employed. As one can see from the figure, the curves 1 and 4 agree satisfactorily at low temperatures (up to the start of sintering). This is explained by the fact that the particles of the fine fraction fill the space in the circumcontact region of the large and medium size particles and, being a significant heat barrier, significantly lower the effective thermal conductivity of the entire fill. Moreover, as the temperature is further raised the finely dispersed particles bring about rapid sintering of the fill, thereby actually playing the role of a special sintering additive [11], and bring about anomalously rapid growth of the effective thermal conductivity (see curve 1 in Fig. 1).

The foregoing analysis leads to the conclusion that the thermal conductivity of a monofraction fill with different chemical-mineral composition with grain sizes exceeding 0.5 mm not studied experimentally, can be predicted based on the indicated model. Figure 4 shows the results of computer calculations of the thermal conductivity of corundum, dinas, and some other refractory fills. These data are obviously of interest in themselves as recommended handbook data and can be employed in heat calculations.

Thus, in this work we have checked experimentally the model of thermal conductivity of granular systems with different composition and structure in the temperature range 500-2000 K. It was shown that the model can predict the thermal conductivity of monofraction, diffi-

cult to sinter, refractory fills with grain sizes of $0.5 \leq d \leq 10$ mm in the range of temperatures at which they are employed. It was shown experimentally that repeated heating up to 2000 K of magnesia, corundum, and other fills increases the initial values of the thermal conductivity by 10-15%, while heatings up to 1500 K have virtually no effect on the initial values of the thermophysical properties. The presence of a fine fraction, with a grain size of the order of 1 μm, in the fill brings about intense sintering and significantly changes the thermal conductivity even at moderate ($\sim$ 1200 K) temperatures.

NOTATION

λ, thermal conductivity; λ_{eff}, effective thermal conductivity of the fill; t, temperature, $T = t + 273.13$; d and r, average diameter and radius of the particles; ρ_b, bulk mass of the fill; m_2, porosity of the system; σ, rms deviation; k, correlation coefficient; λ_s, thermal conductivity of the fill particles; λ_g, thermal conductivity of the gas; h_r, average height of the irregularities of the particles; y_1, y_2, y_3, y_4, geometric parameters of the model; Φ, function describing the spreading of the heat flow; ρ_s, apparent density of the solid fill particles; c_p and c_V, heat capacity of the gas at constant pressure and volume; N_c, coordination number; α, coefficient of accommodation of the gas molecules; p and p_0, pressure of the gas in the experiment and under normal conditions; Λ_0, mean-free path length of gas molecules at normal pressure; Pr, Prandtl number; p_{sp}, external specific pressure on the contact (for free fill $p_{sp} = 0$); h_ℓ, half-height of the fill layer; ε, emissivity of the particles; and $\sigma_{S\text{-}B}$, Stefan–Boltzmann constant.

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