INVESTIGATION OF THE THERMOPHYSICAL PROPERTIES OF FIRECLAY CERAMICS IN THE TEMPERATURE RANGE 80°–1200° K

L. L. Vasil'ev and Yu. E. Fraiman

Inzhenerno-Fizicheskii Zhurnal, Vol. 9, No. 6, pp. 762–767, 1965

UDC 536.212

The thermal conductivity, diffusivity, and specific heat of fireclay ceramics have been investigated over a wide temperature range in various gases. A method of calculating the thermophysical properties of the materials is given, whose use is fully justified by experiment. A method is described of theoretically determining the thermophysical properties of ceramics in various gases on the basis of investigations of these materials in air.

Modern technology makes wide use of ceramics for thermal insulation over a large temperature range, in conditions where the temperature of the surrounding medium varies sharply, in conditions of transpiration cooling, etc. Fireclay ceramics constitute about 40% of manufactured refractories and it is naturally important to know their thermophsical properties over a wide temperature range. A number of papers have been devoted to a study of the influence on the effective thermal conductivity of ceramics of such factors as chemical composition of the skeletal material, porosity, temperature, radiation, convection and the heat conductivity of the gas in the pores. Without listing all the sources, we refer to [1] which gives a detailed survey of the literature on this topic, and also to [2, 3].

The present paper attempts to calculate the temperature dependence of the effective thermal conductivity of ceramics, and to compare the values obtained with experimental results, on the basis of published formulas, the known chemical composition of the ceramic, the temperature dependence of the thermal conductivities of its components, and the experimentally determined porosity.

The material chosen for investigation was 75% fireclay, 12.5 kaolin, 12.0 Latna clay, and 0.5% water-glass. The fireclay was obtained by firing Latna clay. Data on the chemical composition of Latna clay and Glukhov kaolin are given in [4]. The basic chemical constituents of the ceramic are SiO_2 in the amorphous phase and Al_2O_3 in the crystalline. An insignificant portion by volume of the mixture is Fe_2O_3, TiO_2, and CaO. The calculated composition of the ceramic skeleton (% by weight) is as follows: SiO_2—56.1, Al_2O_3—40, Fe_2O_3—1.1, TiO_2—2.1, CaO —0.7. On the basis of literature values of the density of the above chemical compounds, the following chemical composition (volume %) of the ceramic skeleton was determined: SiO_2—64.5, Al_2O_3—32.8, Fe_2O_3—0.6, TiO_2—1.5, CaO—0.6. It is assumed in the later calculations that the ceramic skeleton consists of only two components, SiO_2 and Al_2O_3.

The porosity was determined as follows: a ceramic specimen was kept in a vacuum (1.33 N/m^2) for two days, and then the vessel with the specimen was filled with benzine. The specimen was weighed before and after this procedure. The open porosity found from the weight difference was 40%.

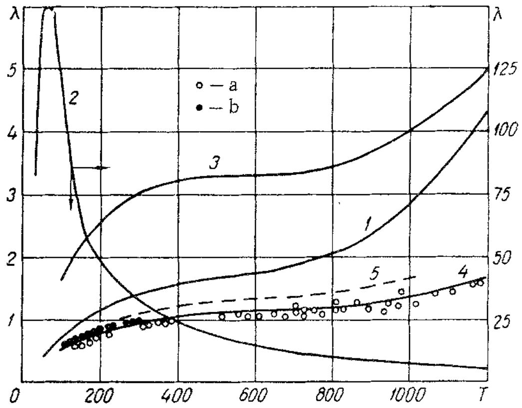

Fig. 1. Values of thermal conductivity λ (W/m · degree) of the ceramic and its components: 1) experimental curve for SiO_2 [6, 9, 10]; 2) experimental for Al_2O_3 [11, 12]; 3) calculated for λ_{sk}; 4) and *a*) calculated and experimental values respectively, of λ_{eff} in air (p = 0.993 · 10^5 N/m^2); 5) and b) calculated and experimental values, respectively, of λ_{eff} in helium (p = 0.993 · · 10^5 N/m^2).

Experiments to determine the thermophysical properties in the temperature range 80°–500° K were carried out by the method described in [6], and in the temperature range 500°–1200° K by the method described in [7]. The low-temperature equipment was a cryostat comprising a vacuum system, an adiabatic calorimeter, and automatic equipment for measuring and controlling the temperature over a wide range. This enabled experiments to be conducted in gases (helium, air, and freon 12) at normal and reduced density (to 0.133 N/m^2). The specimens examined were in rod form (L = 130 mm, d = 40 mm), were surrounded by an adiabatic shell, cooled by liquid nitrogen, and then heated by a constant power source. Specimen temperature was measured by means of copper-constantan thermocouples. During heating of the specimen (the time to carry out the experiment in the temperature range 80°–500° K was 5–7 hr), a determination was made of the temperature dependence of the thermophysical properties of the test material every 3–5°, i.e., up to 80–100 independent values of *a*, λ, and c were obtained in the

Calculated and Experimental Values of λ as a Function of Temperature

T, °K	$\lambda_{Al_2O_3}$	λ_{SiO_2}	λ_{sk}	λ_{gas}	λ_{eff}^{calc}	λ_{eff}^{exp}
Helium, p = 0.993 · 10^5 N/m^2						
40	70.0	0.25	0.58	0.034	0.22	—
100	120.0	0.63	1.52	0.070	0.56	0.55
180	50.0	0.98	2.22	0.097	0.83	0.82
220	43.7	1.10	2.50	0.108	0.90	0.91
300	32.5	1.28	2.85	0.112	1.05	0.95
340	28.5	1.33	3.00	0.165	1.16	0.99
Freon 12, p = 0.993 · 10^5 N/m^2						
300	32.5	1.28	2.85	0.0105	0.90	0.81
340	28.5	1.33	2.85	0.0121	0.91	0.84
Air, p = 0.133 N/m^2						
300	32.5	1.28	2.85	0.9	0.90	0.81
400	23.5	1.50	3.11	—	1.02	0.85
Air, p = 0.993 · 10^5 N/m^2						
100	120.0	0.63	1.52	0.0092	0.50	0.51
180	50.0	0.98	2.25	0.0163	0.73	0.71
220	43.7	1.10	2.50	0.0190	0.81	0.80
300	32.5	1.28	2.85	0.0260	0.94	0.86
400	23.6	1.53	3.24	0.0340	1.08	0.96
600	14.3	1.72	3.28	0.0460	1.10	1.03
800	10.0	2.05	3.46	0.0574	1.17	1.13
1000	7.7	2.91	4.06	0.0684	1.38	1.32
1200	6.3	4.40	4.98	0.0777	1.68	1.57

above temperature range. The error in determining the thermophysical properties was 5%.

The high-temperature equipment was an oven with Silit heaters in which the cylindrical specimen (L = 110 mm, d = 30 mm) was placed, with a constant-power heating source along its axis. In the quasi-steady heating regime, when the temperature of the surrounding medium was varied at constant rate, the effective thermal diffusivity of the ceramic was determined by measuring the temperature differences between two points along the radius of the cylinder using chromel-alumel thermocouples, with the axial heater off, while the effective thermal conductivity was determined by measuring the temperature difference between the same two points, but with the heater on, at a recorded power level. The error in determining a was 5%, and λ—8%.

The effective thermal conductivity was calculated as follows. The conductivity of the ceramic skeleton was determined using the Maxwell-Euken relation, applied to a two-component system in which the particles of the phase smaller by volume are dispersed in a continuous medium [2, 3]:

$$\lambda_{sk} = \lambda_c \frac{1 + 2V_d(1-\lambda_c/\lambda_d)/(2\lambda_c/\lambda_d+1)}{1 - V_d(1-\lambda_c/\lambda_d)/(2\lambda_c/\lambda_d+1)} . \tag{1}$$

To calculate the effective thermal conductivity of the ceramic, the method used was that developed by Dul'nev for determination of the effective thermal conductivity of a two-component system with communicating pores. The author derived the following equation [5] from analysis of the model:

$$\frac{\lambda_{eff}}{\lambda_{sk}} = \left(\frac{h}{L}\right)^2 + \nu\left(1 - \frac{h}{L}\right)^2 + \frac{2\nu h/L(1-h/L)}{1 - h/L(1-\nu)} , \tag{2}$$

which was also used to calculate the effective thermal conductivity of fireclay ceramic.

It is known that heat transfer in the pores of the material under the action of a temperature gradient may arise from radiation from the walls of the pores, and conduction and convection in the pore gas. Depending upon the geometrical pore size, and the mean free path of the gas molecules in the pores, either heat transfer by conduction and convective circulation of the gas in the pores or molecular-viscous gas flow accompanied by effective slip relative to the pore walls may predominate. Analysis of the curve of pore distribution with diameter in the fireclay ceramic investigated showed that the dominant pore diameters are 2–5 μ. If the radiative thermal conductivity is determined for these diameters according to the formula [1]

$$\lambda_r = 2\varepsilon^2 C T^3 d, \tag{3}$$

where d is the pore diameter, it is not hard to verify that it is a fraction of a percent of the conductivity of the gas in the pores of the material in the entire temperature range investigated. For these pore diameters and the comparatively small temperature gradients occuring in the material during the experiments, we may neglect, to an accuracy permissible for engineering calculations, the effects of convective circulation of the gas in the pores [1], and to determine the heat transfer in the pores of the ceramic we may use tabulated values of the thermal conductivity of various gases, given in [8], allowing for pressure.

Let us now turn to a real and interesting point stemming from the analysis of (2). It is evident that if the value of λ_{eff} of the material is determined experimentally, for example, in air, then, knowing the porosity of the material, we may find from (2) the thermal conductivity of the skeleton of the porous material. From knowledge of λ_{sk} and λ for any other gas in the pores of the material, we may calculate λ_{eff} in the atmosphere of this gas. It should be pointed out that most equipment used for determination of thermophysical properties in the temperature range 400°–1200° K is not provided with a vacuum system, and therefore should not be used for investigations in various gaseous media. Calculations of this type may considerably extend investigations of the thermophysical properties of porous materials used in atmospheres other than air. If, in addition, we know the temperature dependence of the specific heat of the material or its thermal diffusivity in air, then the foregoing reasoning is also valid for determining the temperature dependence of the effective diffusivity of the porous material in an atmosphere of different gases. In other words, by experimentally finding the temperature dependences of thermal conductivity and specific heat (or diffusivity) of a porous material in air, knowing its porosity, we can calculate the temperature dependence of λ_{eff} and a_{eff} in any other gas. Calculations and corresponding experiments confirm this conclusion.

Experimental and calculated values of the thermal conductivity of the components of the ceramic, and of its effective thermal conductivity in various gases are given in the table. It may be seen that the calculated values of λ_{eff} are somewhat greater than the experimental. As pointed out in [2], fireclay ceramics have mainly communicating (open) pores. Additional calculations carried out using specific weights and volume ratios of the components indicate that there are about 4% of closed pores. The presence of these pores, of course, lowers the effective thermal conductivity of the ceramic.

It should be noted also that the greatest divergence of the calculated values of λ_{eff} from the experimental data is typically for Freon 12, i.e., a gas whose molecular mean free path ($\bar{l} = 0.024\ \mu$) is less than that of air ($\bar{l} = 0.06\ \mu$), and even more so for helium ($\bar{l} = 0.2\ \mu$). From [13] we may suppose that for freon 12 and to some extent for air, there is a directed flow of gas in the ceramic, arising from the pressure gradient, generated by the temperature gradient, which also reduces (by up to 10%) the effective thermal conductivity of the ceramic in an atmosphere of these gases.

Experimental curves are given in Fig. 1 for the temperature dependence of thermal conductivities of the components, as are the calculated curve of effective conductivity of the ceramic in air and experimental data (points) for the ceramic in air. A calculated curve is also shown for the effective thermal conductivity of the ceramic in helium, constructed on the basis of experiments in air at temperatures of 400°–1000° K. This shows good agreement with experimental data obtained in helium at temperature 80°–350° K.

The experimental data (Fig. 2) on effective thermal diffusivity of the ceramic in helium in the temperature range 100°–350° K show good agreement with the calculated curve constructed from experimental data on the specific heat of the ceramic in the temperature range 80°–1200° K and from calculated data on its effective thermal conductivity in helium.

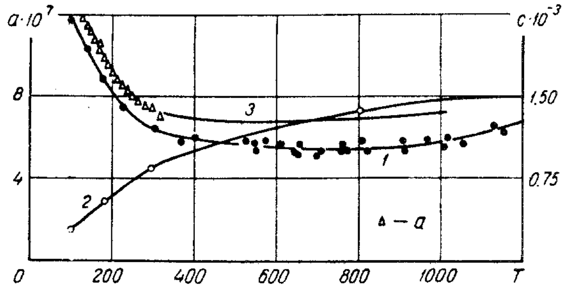

Fig. 2. Values of effective thermal diffusivity a (m^2/sec) and specific heat c (J/kg · degree) of fireclay ceramic: 1) experimental value of λ_{eff} in air; 2) experimental value of c; 3) and a) calculated and experimental values of a_{eff} in helium.

NOTATION

λ_{eff}) effective thermal conductivity of porous material; λ_{sk}) thermal conductivity of skeleton; λ_c) thermal conductivity of continuous phase of skeleton; λ_d) thermal conductivity of dispersed phase of skeleton; V_d) volume fractions of disperse phase of skeleton; P) volume porosity, $h/L = f(P)$ [5]; c) Stefan-Boltzmann constant; T) absolute temperature, °K; d) pore diameter; a) thermal diffusivity.

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26 February 1965

Heat and Mass Transfer Institute
AS BSSR, Minsk