# ON THE TEMPERATURE DEPENDENCE OF THE THERMAL CONDUCTIVITY OF CERAMIC MATERIALS WITH RAREFACTION OF THE GAS MEDIUM

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The results of an experimental study of the temperature dependence of the thermal conductivity of ceramic materials under conditions of rarefaction of the gas medium are explained by processes of degassing of the material during the experiment.

Experimental studies [1, 2] show that the thermal conductivity of refractory materials based on aluminum and magnesium oxides in a vacuum differs sharply from the data at normal pressure not only in absolute value but also in the nature of the temperature dependence. In particular, according to [1, 2] the thermal conductivity of corundum and magnesite ceramic displays a positive temperature coefficient at a pressure of the external medium of $10^{-4}$ mm Hg and at low temperatures. At increased temperatures a breakdown in the monotonic nature of the curve of thermal conductivity of magnesite ceramic is observed under conditions of the same pressure of the external medium. The latter is confirmed by our data, obtained on an instrument described in [3] (Fig. 1a).

Attention must also be drawn to the hysteresis in the temperature dependence of the thermal conductivity of magnesite ceramic (Fig. 1a). The data obtained during heating of the samples are located above the values of the thermal conductivity measured during cooling.

Interpretation of these facts on the basis of the known methods of calculation is not successful. The best results (Fig. 1a, b) are obtained with calculation by the equation proposed in [4]. At the same time, calculation by this equation does not give the nature of the temperature dependence of the thermal conductivity with rarefaction which was discovered experimentally. The growth in thermal conductivity with

TABLE 1. Calculation of Pressure in Pores of Corundum Ceramic at an External Pressure of $10^{-4}$ mm Hg

| $T$, °C | 200 | 400 | 600 | 800 | 900 | 1000 | Source | Note |
|---|---|---|---|---|---|---|---|---|
| $\lambda_{exp}$, W/m·deg | 1,1 | 1,15 | 1,25 | 1,50 | 1,68 | 1,86 | [2] | |
| $\lambda_{sk}$, W/m·deg | 22,4 | 13,1 | 9,12 | 7,21 | 6,68 | 6,16 | [15] | |
| $M$ | 0,102 | 0,183 | 0,28 | 0,434 | 0,526 | 0,63 | | |
| $\bar{\lambda}_\delta \cdot 10^4$ | 0,12 | 1 | 4,5 | 7,5 | 9,2 | 15 | | |
| $\bar{\lambda}_\delta \cdot 10^4$, W/m·deg | 2,15 | 6,3 | 19,5 | 25,9 | 29,5 | 44,4 | | |
| $\Pi \cdot 10^5$, N/m·deg | 7,4 | 7,35 | 7,1 | 6,95 | 6,90 | 6,88 | | $\delta = 10^{-7}$ m<br>$L = 10^{-4}$ m<br>$\bar{a} = 0,05$<br>$P = 24\%$<br>$f(P, \nu) = 0,48$ |
| $\lambda_0 \cdot 10^3$, W/m·deg | 39,4 | 52 | 62,5 | 71,6 | 76,6 | 79,6 | [18] | |
| H, mm Hg | 14,4 | 45,2 | 145 | 210 | 242 | 388 | | |

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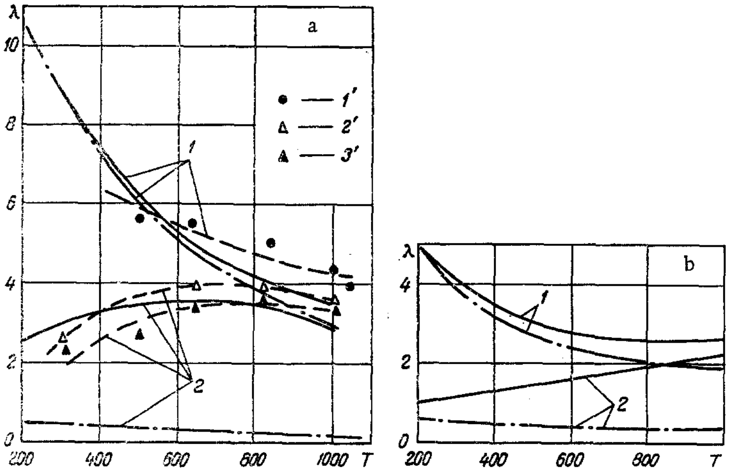

Fig. 1. Thermal conductivity of magnesite (a) and corundum (b) ceramic at different pressures (W/m • deg): 1) 760 mm Hg; 2) $10^{-4}$; 1') 760; 2') $10^{-4}$ (during heating); 3') $10^{-4}$ (during cooling). Solid curves are experimental data of [1], dashed curves are authors' experimental data, and dash–dot curves are calculated functions (without allowance for degassing).

rarefaction is explained in [1, 2] by an increase in the radiant component of heat conduction. At the same time, the concrete estimates of [3-7] show that because of the small size of the microcracks the radiant component does not make a significant contribution to the effective thermal conductivity, especially for dense refractory materials. The change in the monotonic nature of the thermal conductivity curve (Fig. 1a) is not even discussed in [1-2].

In the present report an attempt is made to explain the temperature dependence of the thermal conductivity with rarefaction of the gas medium by processes of gas release from the ceramic.

It is known [8, 9] that there is a large amount of absorbed gas in ceramic materials. This gas is released during heating and can alter the pressure by an order of magnitude or more in an evacuated volume of the test samples. Besides the absorbed and adsorbed gas, with a decreased partial oxygen pressure and an increase in temperature a powerful source of gas release is the dissociation of oxides of variable valency, in particular $Fe_2O_3$, $TiO_2$, etc. [10], of which there are usually admixtures in refractory materials [11]. In particular, during the heating of magnesite ceramic under conditions of rarefaction it whitens, which is connected with the conversion of admixtures of $Fe_2O_3$ into FeO. In connection with the above it can be assumed that because of the great hydraulic resistance of the fine pores and microcracks, the pressure in them differs considerably from the pressure in the volume of the vacuum chamber. In the presence of a large reserve of absorbed gas in the solid phase of the ceramic and with a constant external pressure, the pressure in the pores may remain constant for a long time. We note that in this case the pressure in the fine pores and microcracks at the contact between particles can be considerably greater than in the large pores which have relatively low hydraulic resistance. Below an attempt is made to estimate the pressure in the microcracks.

Let us assume that the disagreement in the calculated and experimental curves of thermal conductivity (Fig. 1a, b) is entirely due to the incorrect estimate of the pressure in the microcracks. One can calculate the pressure for the condition of agreement of calculation and experiment.

Let us dwell in more detail on the course of the calculation. The model and calculating equation proposed in [4] is taken as the basis. The equation for the efficiency of heat conduction can be represented in the following form:

$$\lambda = M\lambda_{sk} f(P, \nu). \tag{1}$$

The function $f(P, \nu)$ in the case of open porosity must be calculated from G. N. Dul'nev's equation [12]. The parameter M is a function of the parameters of the structure and the thermal conductivity of the gas

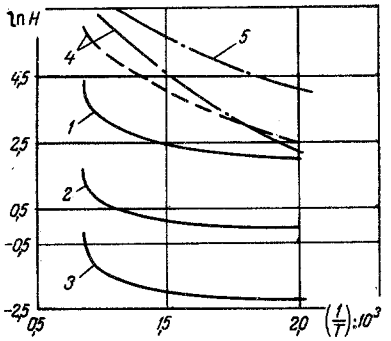

Fig. 2

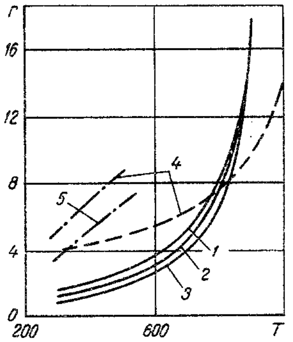

Fig. 3

Fig. 2. Temperature dependence of pressure in microcracks of refractory ceramic at different external pressures: 1) 6 mm Hg; 2) 1; 3) $10^{-1}$; 4) $10^{-4}$; 5) 760. Solid curves are ShLB-0.4; dashed curve is corundum ceramic; dash–dot curve is magnesite ceramic.

Fig. 3. Dependence of activation energy on temperature at different external pressures (kcal/mole): 1) 6 mm Hg; 2) 1; 3) $10^{-1}$; 4) $10^{-4}$; 5) 760. Solid curves are ShLB-0.4; dashed curve is corundum ceramic; dash–dot curve is magnesite ceramic.

$$M = M(\bar{a},\ \bar{\lambda}_\delta \bar{\delta}). \tag{2}$$

The thermal conductivity $\lambda_\delta$ of the gas in the microcracks is connected with the pressure H and the thickness $\delta$ of the microcracks by the equation [13]

$$\lambda_\delta = \frac{\lambda_0}{1 + \frac{\Pi T}{H\delta}}, \tag{3}$$

where

$$\Pi = \frac{4c_p/c_v\,(2 - A)\,K}{(c_p/c_v + 1)\,A\,\mathrm{Pr}\,\sqrt{2}\,\pi\sigma^2}.$$

The dependence (2) is calculated and presented in the form of graphs in [14]. The calculation was conducted as follows.

The coefficient M was determined from the equation

$$M = \frac{\lambda}{\lambda_{\mathrm{sk}} f(P,\ \nu)}. \tag{4}$$

The thermal conductivity of the material was determined experimentally; the literature data presented in Fig. 1a, b were used in particular. The method of determining $\lambda_{\mathrm{sk}}$ is described in [5, 6]. The parameters of the texture were chosen on the basis of the known data on the structure of refractory materials [11] and from the condition of agreement of calculation and experiment at low temperatures. It can be shown that the accuracy in the choice of the parameters has almost no effect on the error in determining the pressure H. This is connected with the mutual compensation of different systematic errors.

From the values of M found we determined $\bar{\lambda}_\delta$ and

$$\lambda_\delta = \bar{\lambda}_\delta \lambda_{\mathrm{sk}} \tag{5}$$

on the basis of Eq. (2).

Then the pressure H was calculated using Eq. (3).

An example of the calculation of the pressure in the microcracks of corundum ceramic on the basis of the experimental data presented in Fig. 1b is presented in Table 1. The calculation was conducted with the parameters $\delta = 10^{-7}$ m, $L = 10^{-4}$ m, $\bar{d} = 0.05$, and $P = 24\%$.

As seen from Table 1, the pressure in the pores increases with temperature and differs by several orders of magnitude from the pressure in the chamber. Similar results occur for other refractory materials (Fig. 2), in particular the ultralight-weight ShLB-0.4 brick with a porosity of 80%.

An explanation for the breakdown of the monotonic nature of the $\lambda(T)$ curve for magnesite refractory materials can be given on the basis of the hypothesis of a pressure difference between the pores and the external medium. The pressure in the pores increases with an increase in temperature, which corresponds to a positive temperature coefficient. When the pressure in the microcracks reaches 760 mm Hg the temperature dependence begins to depend mainly on $\lambda_{sk}$, and $\lambda(T)$ has a negative temperature coefficient. The hysteresis in the thermal conductivity (see Fig. 1a) during cooling and reheating is obviously explained by gradual degassing of the ceramic.

The qualitative argument given above indicates an increase in the pressure in the pores, but at the same time it is desirable to have an additional argument for confirmation of the assumption that there is a sharp pressure difference between the microcracks and the external medium. Unfortunately, there are at present no technological means for the direct measurement of the pressure in microcracks. The degassing time for ceramic was estimated on the assumption that the contact between the baked particles represents a system of semiclosed pores having an exit opening $10^{-9}$ m in diameter; each pore can be filled $10^3$ times with gas at normal pressure. The estimates showed that the degassing time is 30 days or more, i.e., in ordinary experiments on thermal conductivity not exceeding 10-15 h the effect of a degassing decrease can be observed in the form of hysteresis in the thermal conductivity, which was discovered (Fig. 1a).

The calculated values of the pressure in microcracks can be justified by methods of thermodynamics by comparing the activation energy of the degassing process with certain data on the energy of desorption of gases from ceramic materials. At low temperatures one can expect values of 2-10 kcal/mole [8, 16] for the energy corresponding to physical desorption; with an increase in temperature the activation energy corresponds to processes of chemosorption and diffusion of 20-100 kcal/mole [16-17].

For the case of equilibrium systems the connection between the gas pressure, temperature, and activation energy of desorption is given by the well-known Clapeyron-Clausius equation. We can show that an analogous equation is valid in our case.

Let us consider a system consisting of two phases. We will assign the subscript 1 to the first phase (the gas absorbed on the surface) and the subscript 2 to the second (the gaseous phase). The system is thermostatic, i.e., all the thermal effects are compensated for by an external heat source. We take the temperatures of the two phases as equal ($T_1 = T_2 = T$). The pressures of the phases are $H_1$ and $H_2$. A flow of gas from phase 1 to phase 2 occurs in connection with the pressure drop. The steadiness of the pressures is assured by the large reserve of gas in the ceramic and by communication with the external medium to which the gas is drawn off. Let us write equations for the thermodynamic (chemical) potentials of the two phases:

$$\begin{aligned} Z_1 &= U_1 - TS_1 + H_1V_1, \\ Z_2 &= U_2 - TS_2 + H_2V_2. \end{aligned} \tag{6}$$

We assume that

$$\begin{aligned} H_1 &= H - \Delta H_1, \quad \Delta H_1 = \text{const}, \\ H_2 &= H - \Delta H_2, \quad \Delta H_2 = \text{const}, \end{aligned} \tag{7}$$

where H is the equilibrium pressure corresponding to the temperature T. Then

$$\begin{aligned} Z_1 &= U_1 - TS_1 + HV_1 - \Delta H_1V_1, \\ Z_2 &= U_2 - TS_2 + HV_2 - \Delta H_2V_2. \end{aligned} \tag{8}$$

Because of Eqs. (7) we have

$$dZ_1 = dZ_2, \tag{9}$$

i.e.

$$-S_1dT + V_1dH = -S_2dT + V_2dH,$$

$$\frac{dH}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{r}{(V_2 - V_1)T}. \tag{10}$$

The pressure H is unknown, and at the same time it follows from the conditions (7) that

$$\frac{dH_2}{dT} = \frac{dH}{dT}. \tag{11}$$

Neglecting the specific volume of the adsorbed material and using the equation $V_2 = RT/H_2$, we obtain

$$\frac{d\ln H_2}{d(1/T)} = -\frac{r}{R}. \tag{12}$$

Equation (12) is analogous to the Clapeyron–Clausius equation for equilibrium systems. In addition it should be emphasized again that in this equation we use not the equilibrium pressure but the pressure of the gas in the microcrack under conditions of continuous evacuation. Equation (12) is correct when the conditions (7) are satisfied, i.e., when the curves $H_2(T)$ are equidistant under conditions of a different pressure in the vacuum chamber. The latter can serve as a means of experimentally testing the limits of applicability of Eq. (12) for the systems studied. As seen from the experimental curves presented in Fig. 2, the functions $H_2(T)$ are arranged equidistantly for different materials. The phase transition energies (Fig. 3) calculated on the basis of the $H_2(T)$ curves are in satisfactory agreement with the literature data indicated above for heats of desorption.

We note in conclusion that the arguments presented provide a basis for considering the hypothesis that the temperature dependence of the thermal conductivity under conditions of rarefaction of the external medium is connected with processes of degassing of the ceramic as sufficiently justified.

## NOTATION

$\lambda$, $\lambda_{sk}$, $\lambda_\delta$: coefficients of effective thermal conductivity and of thermal conductivity of skeleton (solid phase) and microcracks; M: parameter characterizing the effect of microcracks on thermal conductivity; $f(P, \nu)$: function characterizing the effect of open pores (except for microcracks) on thermal conductivity; P: porosity; $\nu = \lambda_2/\lambda_{sk}$; $\lambda_2$: thermal conductivity of gas in pores; $\bar{a} = d/\Delta$: ratio of diameter of contact spot between particles to diameter of particles; $\bar{\delta} = \delta/L$: ratio of thickness of microcracks to distance between microcracks; $\bar{\lambda}_\delta = \lambda\delta/\lambda_{sk}$; $c_p/c_V$: heat capacity of gas at normal pressure and volume; K: Boltzmann constant; A: accommodation coefficient (taken as equal to 1); Pr: Prandtl number; H: pressure in microcracks; $T_1$, $U_1$, $S_1$, $H_1$, $V_1$, $T_2$, $U_2$, $S_2$, $H_2$, $V_2$: temperature, internal energy, entropy, pressure, and specific volume of phases 1 and 2; r: activation energy; R: universal gas constant.

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