

7. P. P. Kulik, in: *Essays in Low-Temperature Plasma Physics and Chemistry* [in Russian], Nauka, Moscow (1971).
8. I. A. Sokolova, in: *Physical Kinetics* [in Russian], ITPM SO AN SSSR, Novosibirsk (1974).
9. J. N. Butler and R. S. Brokaw, *J. Chem. Phys.*, **26**, No. 6 (1957).
10. J. N. Yos, "Revised transport properties of high temperature air and components," *AVCO Trans.* (1967).
11. J. A. Fay and F. Riddell, *J. Appl. Spectrosc.*, No. 2 (1958); *Problems of the Motion of Long-Distance Rocket Nosecones* [Russian translation], IL, Moscow (1959).
12. O. N. Suslov, *Zh. Prikl. Mekh. Tekh. Fiz.*, No. 3 (1972).

RELATIONSHIP OF GAS PHASE MASS TRANSFER TO THERMAL CONDUCTIVITY OF REFRACTORIES

E. Ya. Litovskii, F. S. Kaplan,
and A. V. Klimovich

UDC 536.21

The problem of change in thermal resistance of pores and microcracks in refractories with occurrence of heterogeneous reactions and formation of gas with diffusion product transfer in the temperature gradient field is analyzed.

It has been demonstrated previously [1-3] that thermal resistance of the microcracks which have a marked influence on effective thermal conductivity and diffusivity of ceramics, refractories, and other porous materials is related to, among other factors, the intensity of mass-transfer processes in the gas phase. Such a process develops in microcavities filled by gas in the presence of a temperature gradient and is caused by the temperature dependence of equilibrium pressure of the gaseous products formed by heterogeneous chemical reactions and phase transformations. In this case the effective thermal conductivity of the microcracks must be supplemented by a term related to mass transfer:

$$\lambda = \sum_i j_i H_i \frac{\delta}{\Delta T}, \quad (1)$$

where j_i is the molar flow of the i -th gaseous component, H_i , its enthalpy; δ , gap thickness; ΔT , temperature change.

In [3] expressions were obtained for the effective mass flow and effective thermal conductivity of a microcrack for free-molecular (Knudsen) gas flow (λ^{Kn}). Such a regime is realized at high rarefactions in narrow gaps. However, it follows from analysis of the structure of many refractories that they contain a significant quantity of coarse pores and cracks, where at pressures of 10^2 - 10^5 N/m² gas product transfer is accomplished basically due to diffusion. The effective thermal conductivity of a microcrack in the diffusion regime λ^D is determined by the temperature and thermodynamic properties of the system, and in contrast to the parameter λ^{Kn} it is dependent on the diffusion coefficients of the molecules, their concentrations, the total gas pressure p , and the relationship between the flows j_i . In the simplest case of a binary mixture consisting of an "active" substance, i.e., one which liberates gas during a heterogeneous reaction or phase transition, and a "passive" gas, i.e., one not participating in these processes, the expression for λ^D has the form

$$\lambda^D = \frac{p p_A}{p - p_A} \cdot \frac{(\Delta H)^2}{R^2 T^3}, \quad (2)$$

where $D \sim p^{-1}$ is the binary diffusion coefficient; $p_A \sim \exp(-\Delta H/RT)$ is the pressure of active gas; ΔH , thermal effect of the process; R , gas constant; $T = \sqrt{T_1 T_2}$ (T_1 and T_2 are temperatures of hot and cold surfaces).

Equation (2) was obtained by solution of the diffusion equation in a plane-parallel gap with consideration of the Stefan flow [4], assuming the process occurs in equilibrium and that $\Delta T \ll T$. It is analogous to the expression for thermal conductivity of a chemically reacting gas mixture of [5], differing only by the factor $p_A/p - p_A$ produced by the Stefan mass flow.

All-Union Institute of Refractories, Leningrad. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 34, No. 3, pp. 452-455, March, 1978. Original article submitted March 9, 1977.

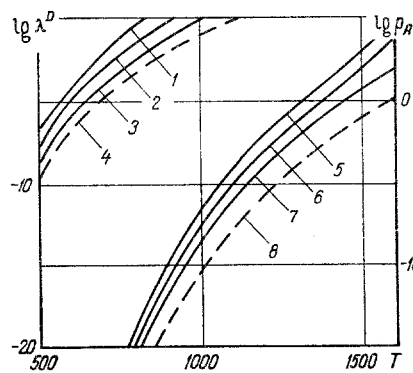


Fig. 1

Fig. 1. Effective gap thermal conductivity λ^D W/m \cdot K (1-3, 5-7) and equilibrium pressure p_A N/m 2 (4, 8) versus temperature T, $^{\circ}$ K for following reactions on gap walls, $\text{CaCO}_3\text{T} \rightleftharpoons \text{CaO}_\text{T} + \text{CO}_2\text{T}$ (1-4) and $2\text{Fe}_2\text{O}_3\text{T} \rightleftharpoons 4\text{FeO}_\text{T} + \text{O}_2\text{T}$ (5-8). Pressure of passive gas (nitrogen): $1.3 \cdot 10^3$ N/m 2 (1, 5); $1.3 \cdot 10^4$ N/m 2 (2, 6); curves 3 and 7 calculated for case where total gas pressure $p = p_A + p_p(\text{N}_2) = 10^5$ N/m 2 .

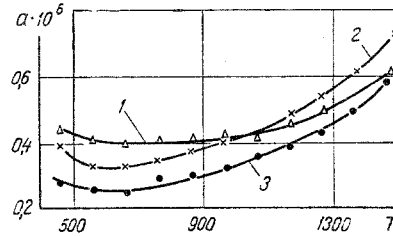


Fig. 2

Fig. 2. Thermal diffusivity of lightweight refractory ShLB-0.6 versus temperature for nitrogen pressures of 10^5 N/m 2 (1); $8 \cdot 10^2$ N/m 2 (2); and $1.3 \cdot 10^2$ N/m 2 (3); $a \cdot 10^6$ m 2 /sec; T, $^{\circ}$ K.

Figure 1 shows the temperature dependence of the quantity λ^D as calculated by Eq. (2) for reactions on the gap walls which are characteristic of real refractories. The values of ΔH and p_A were calculated from the thermodynamic data of [6], and the D values were obtained from [7]. Analysis of the function $\lambda^D = f(T)$ shows a significant growth in effective thermal conductivity of microcracks and pores (and, consequently, of the material itself) with increase in temperature, which is related to the exponential dependence of $p_A(T)$. At the same time, the reduction in passive gas pressure p_p should be accompanied by an increase in thermal conductivity of the material since $\lambda^D \sim p_A/p_p$. Such an effect has been observed experimentally in studies of the thermal properties of refractories containing many coarse pores. As an example, Fig. 2 shows thermal-diffusivity measurements performed on the lightweight refractory ShLB-0.6.* The apparent density of the material was 0.56 g/cm 3 , open porosity, 77.9%; mean pore size, 0.3-1.0 mm; Fe $_2$ O $_3$ content, about 1.6%. Thermal diffusivity was determined by monotonic heating of planar specimens 90 \times 90 \times 26 mm, with temperature measured by VR 5/20 thermocouples and a heating rate of 20 $^{\circ}$ /min. The experimental apparatus and peculiarities of the method used were described in [8]. Curves 2 and 3 were obtained for pressures of $\sim 10^3$ N/m 2 and $\sim 10^2$ N/m 2 (at temperatures above 1000 $^{\circ}$ K), which correspond to free path lengths of $\sim 10^{-2}$ mm and $\sim 10^{-1}$ mm, i.e., even at the lowest experimental pressures the diffusion regime of gas flow is realized in the material pores. Results of repeated measurements for the high-temperature portion of the curves differed by 3-5%, which lies within the limits of the method's error.

The experimental data of Fig. 2 may be explained as follows. At low temperatures where the active gas pressure is low, the decrease in total pressure p must be accompanied by increase in thermal resistance of the pores and microcracks and a corresponding drop in effective thermal conductivity of the material (Fig. 2, curves 1-3 in the range 500-800 $^{\circ}$ K) [9]. Further temperature increases lead to an abrupt rise in p_A , so that the contribution of λ^D to total thermal conductivity of the gas-filled cavities proves to be significant. This contribution is all the more noticeable, the lower the pressure of the passive gas (see Fig. 1). Thus, the more rapid temperature increase of effective thermal conductivity of ceramics upon rarefaction is explained (Fig. 2 at temperatures above 900 $^{\circ}$ K). Here, as in the Knudsen regime of gas flow [3], the thermal conductivity of the evacuated material approaches that at atmospheric pressure with increase in temperature (curves 2, 3) and even exceeds it somewhat (curve 2). It is necessary, however, to consider the possibility of intense removal of gaseous products from the volume of the coarse-pored material into the space surrounding the specimen, which will be accelerated with decrease in pressure in the vacuum chamber. If the rate of active gas removal exceeds its formation rate, then the quantity p_A , and with it, λ^D will decrease, which is evidently the cause of the form of the high-temperature portion of curve 3 in Fig. 2.

*Ya. A. Landa and N. A. Puchkevich participated in the measurements.

It should be stressed that in the general case the growth of thermal diffusivity of real materials does not correspond not to such an intense increase in thermal conductivity of pores and microcracks as follows from Eq. (2) and the reactions considered. In fact, upon decomposition of Fe_2O_3 the thermal conductivity of the pores should reach that of the solid phase at a temperature of $\sim 1600^\circ\text{K}$, while for CaCO_3 decomposition this should occur as low as $800\text{--}1000^\circ\text{K}$, while under real conditions even at higher temperatures the thermal conductivity of porous compositions at pressures of $10^3\text{--}10^5 \text{ N/m}^2$ is still significantly lower. This may possibly be related to the fact that the materials participating in the heterogeneous reaction segregate themselves on grain boundaries and interphase surfaces, so that as a rule they are in a dilute state and rarely comprise a separate phase (solid or liquid) [10]. This fact then causes the pressure p_A in the material pores to be significantly lower than follows from thermodynamic calculations for pure substances. In addition we must keep in view the possibility referred to above of intense removal of the gaseous products into the space surrounding the specimen. For a quantitative calculation it will evidently be necessary to study the kinetics of specimen degasification, the composition of the gas liberated, and the change in specimen structure in the temperature gradient field.

It is important to note that the mechanisms of heat and mass transfer considered here are not specific. The relationships proposed in the present study and in [3] may be used for calculation of contact thermal resistances at the boundary of any solid material in the presence of sorption-desorption, evaporation-condensation, heterogeneous chemical reactions, etc.

LITERATURE CITED

1. E. Ya. Litovskii, in: Summaries of Reports to the Fifth All-Union Conference on Thermophysical Properties of Materials [in Russian], Naukova Dumka, Kiev (1974), p. 28.
2. E. Ya. Litovskii, I. D. Zborovskii, and I. V. Uspenskii, *Inzh.-Fiz. Zh.*, 27, 648 (1974).
3. E. Ya. Litovskii, F. S. Kaplan, and A. V. Klimovich, *Inzh.-Fiz. Zh.*, 33, No. 1 (1977).
4. D. A. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics* [in Russian], Nauka, Moscow (1967).
5. N. Butler and R. Brokaw, in: Problems of the Motion of Long-Distance Rocket Nosecones [Russian translation], IL, Moscow (1959) p.378.
6. I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances*, Springer-Verlag, Berlin-Hamburg-New York (1973).
7. N. B. Vargaftik, *Handbook of Thermophysical Properties of Gases and Liquids* [in Russian], Nauka, Moscow (1972).
8. E. Ya. Litovskii, Ya. A. Landa, and N. A. Puchkelevich, *Tr. Vses. Inst. Ogenupor.*, No. 43, 34 (1971).
9. G. N. Dul'nev, Yu. P. Zarichnyak, and E. Ya. Litovskii, in: *Thermophysical Properties of Solids* [in Russian], Naukova Dumka, Kiev (1971), p. 76.
10. W. D. Kingery, *J. Am. Ceram. Soc.*, 57, 74 (1974).