HETEROGENEOUS HEAT—MASS TRANSFER AND EFFECTIVE THERMAL CONDUCTIVITY OF PORES IN CERAMIC MATERIALS AT ARBITRARY KNUDSEN NUMBERS

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Approximate expressions are obtained for mass flux and thermal conductivity component in a temperature gradient field in a plane slit. A number of examples are used to demonstrate the significant contribution of heat—mass transfer in the transitional regime to thermal conductivity of refractory materials.

An analysis of the intensity of heat—mass transfer processes within the pores and microfissures of refractory materials upon evaporation, dissociation, and other heterogeneous physicochemical processes is of practical importance since in the operation of thermostable materials under conditions characteristic of present day technology, i.e., in the range of temperatures near the melting point, in various gas media under high and low pressure, and at high thermal flux, such processes lead to marked change in the structure and properties of ceramics.

Heat—mass transfer in pores and microfissures under the influence of a temperature gradient has been studied previously [1] for the case of free molecular and diffusion motion of gas molecules. However, the structure of the pore space of the majority of refractory materials is such that an intermediate regime of gas motion is usually to be found in the pores. Therefore, study of heat—mass transfer over a wide Knudsen number range is of practical interest. The most systematic approach to this problem commences from the Boltzmann kinetic equation. However, the difficulties which arise in studying the kinetic equation in multicomponent systems [2] and the absence of data on the concrete parameters of gas molecule interaction with the solid surface and each other compel us to obtain interpolation formulas, considering both the limiting regimes examined previously and certain results of solution of the kinetic equation obtained for recondensation of a single-component gas. Such an approach was applied to an analysis of heat—mass transfer in ice sublimation in a rarefield atmosphere [3]. On the basis of gas kinetic theory, the authors attempted to represent the resistance to heat—mass transfer in a gap in the form of the sum of three resistances: two free molecular, localized at the solid surfaces at the mean free path length distance (Λ), and a diffusion component, located in the middle of the gap. Such a model describes experimental results [3] satisfactorily at $\mathrm{Kn} < 10^{-2}$. However, as can easily be shown, it will not describe the limiting transition to free molecular flow as $\mathrm{Kn} \to \infty$; if $\mathrm{Kn} > 2$, the calculation formula loses its meaning, since the diffusion resistance to transfer becomes negative.

In constructing interpolation formulas applicable to analysis of the heat—mass transfer processes in ceramic microfissures for the case of arbitrary Kn values, we have also assumed that the total resistance to heat—mass transfer can be represented as the sum of consecutively situated resistances. However, in order that the calculation formula should satisfy limit relationships, it proved sufficient to assume the existence of only two (and not three, as in [3]) resistances: free molecular and diffusion. To find the mass flux it is necessary to be able to calculate each component of the total flux individually. For a constant concentration gradient the diffusion resistance must depend on the gas molecule motion regime, i.e., on the value of Kn. In fact, it follows from elementary gas kinetic theory [4] that the probability of scattering of molecules in a gap f is equal to $1 - e^{-1/\mathrm{Kn}}$. Therefore, the value of R_D will be directly proportional to not only the thickness of the gap, but also to the quantity f. Although molecular collisions hindering free mass transfer

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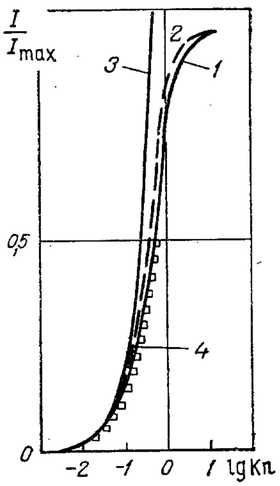

Fig. 1

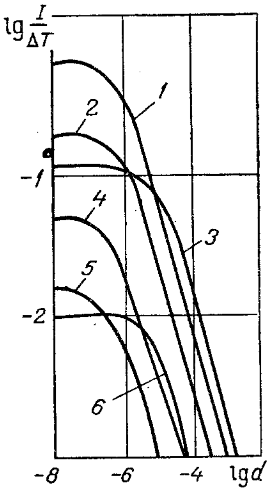

Fig. 2

Fig. 1. Quantity I/I_{max} vs log Kn for decomposition of $CaCO_3$ at T = 800°K, calculated by Eq. (2) (curves 1, 2), by Stefan's formula (3) and from equation of [3] (4). "Passive" gas (nitrogen) pressure, Pa: $1.3 \cdot 10^2$ (curve 2); $1.3 \cdot 10^3$ (curves 1, 3, 4).

Fig. 2. CrO_3 flux, mole/m^2·sec·deg K vs microfissure size, m, for various partial oxygen and total pressures, Pa: 10^5 and 10^5 (curves 1, 4); 2.10^4 and 10^5 (2, 5); 10^4 and 10^4 (3, 6); curves 1-3 are for T = 2200°K; 4-6, for T = 1600°K.

and leading to diffusion occur with equal probability at any point in the gap, for calculation of R_D it will be convenient to introduce an effective diffusion length $d_1 = df$, where d is the gap thickness. We will now concentrate the diffusion component at one of the surfaces, assuming the diffusion length equal to d_1, and further assuming that in the remaining portion of the gap free molecular mass transfer occurs, with the resistance to transfer determined solely by the difference in pressure of the "active," i.e., transferred gas. Then the total resistance $R = R_{Kn} + R_D$, and as $Kn \to \infty$, $d_1 \to 0$ $R \to R_{Kn}$, while for $Kn \to 0$, $d_1 \to d$ $R \to R_D$, i.e., this relationship satisfies the known limiting cases. In the case of a developed hydrodynamic regime of gas recondensation at high concentrations of the "active" gas and low concentrations of the "passive" gas, the model is experimentally justifiable [5].

On the basis of such concepts, it is simple to obtain an expression for the gas molecule flux in the gap. To do this it is necessary to solve a system of equations, one unknown in which is the concentration (pressure) of the "active" gas at the boundary between the diffusion and free molecular regions p_{A_1}. For the case of a single component active gas and with some simplifying assumptions, we have

$$\begin{cases} I = \dfrac{2}{\sqrt{2\pi MRT}} (p_{A0} - p_{A1}), \\ I = \dfrac{Dp}{\delta_1 RT} \left(\dfrac{p_{A1} - p_{A2}}{p - p_{A2}} \right), \end{cases} \tag{1}$$

where M is the molecular mass of the active gas; p, total pressure in the gap; p_{A_0} and p_{A_2}, partial pressures of the active gas on the hot and cold surfaces; D, diffusion coefficient; R and T, gas constant and absolute temperature; I, mass flux (mole/m^2·sec). The heat flux Q related to this mass flux will equal I ΔH, where ΔH is the thermal effect of the process.

To analyze the relationships obtained, it will be convenient to consider the dimensionless ratio of the flux value corresponding to a fixed value of Kn to the maximum possible flux I_{max}, realizable in the free molecular regime. For a two-component gas mixture we obtain

$$\frac{I}{I_{\max}}=\left[1+\frac{2d_1RT\,(p-p_{A2})}{Dp\sqrt{2\pi MRT}}\right]^{-1}. \tag{2}$$

Figure 1 shows values of $I/I_{\max}$ calculated by Eq. (2) (curves 1, 2), by Stefan's formula (curve 3), and by the equation of [3] (curve 4) for the reaction of $CaCO_3$ decomposition at $T = 800°K$. It is evident from the figure that Eq. (2) permits calculation of the mass flux at arbitrary Kn, while the expression obtained previously in [3], although giving accurate results up to $Kn < 0.5$, loses meaning at higher values.

Derivation of the expression for effective thermal conductivity of the gap in the transition regime from Eq. (2) is elementary:

$$\lambda=\lambda_{\max}\left[1+\frac{2d_1RT\,(p-p_{A2})}{Dp\sqrt{2\pi MRT}}\right]^{-1}, \tag{3}$$

where the expression for maximum gap conductivity corresponding to free molecular flow mass transfer has the form [1]

$$\lambda_{\max}=\frac{\alpha p_A d_1(\Delta H)^2}{RT^2\sqrt{2\pi MRT}}. \tag{4}$$

Here α is the gas molecule reflection coefficient and ΔH is the heat of the process.

As an example of application of the expressions obtained in analysis of processes within a ceramic, Fig. 2 shows the result of calculation of the mass transfer developing in passage of a thermal flux through chromium oxide refractories in a medium with various partial oxygen pressures. Thermodynamic analysis shows that the main product of Cr_2O_3 interaction with oxygen is the gaseous oxide CrO_3:

$$2Cr_2O_{3\,s}+3O_{2g}\rightleftarrows 4CrO_{3}g.$$

Reaction equilibrium constants, partial CrO_3 pressures at various O_2 pressures, and the reaction thermal effect were calculated on the basis of thermodynamic data, while the diffusion coefficient was found from Gillilend's formula [6]. As follows from the curves presented in Fig. 2, the intensity of mass transfer depends to a significant degree on both the microfissure size, and on the partial oxygen and total gas pressure. In microfissures greater than 10 μm in size, where a diffusion transfer regime is realized at the parameter values considered, the relationship between CrO_3 pressure and the quantity D has its greatest effect. Therefore, upon heating in a rarefied oxidizing atmosphere (curves 3, 6) the CrO_3 flux relative to the temperature head is higher than in air or in pure oxygen. At the same time, in finer pores the mass transfer rate in pure oxygen at atmospheric pressure (curves 1, 4) is significantly higher than in air (curves 2, 5) and in rarefied oxygen (curves 3, 6). We note that at a temperature differential of 0.01°K at $T = 2200°K$ the maximum rate of grain boundary migration comprises 61.7 μm/h, with a thermal flux of 157 W/m^2.

In conclusion, we note that the transition of the mass-transfer regime from diffusion to free molecular (see Fig. 1) corresponds to numbers $Kn \approx 10^{-2}$–10^{1}, which for the dominant intergrain boundary thickness in ceramics of ≈ 1 μm corresponds to pressures of 10^{2}–10^{4} Pa. It is in this range that the main change in thermal conductivity and diffusivity of ceramic materials does occur [7-9], and the transitional mass transfer regime has a significant effect on thermal conductivity of refractories.

LITERATURE CITED

1. E. Ya. Litovskii, F. S. Kaplan, and A. V. Klimovich, "The effect of pore thermal resistance reduction in solids," Teplofiz. Vys. Temp., 15, 913-916 (1977); "Relationship of diffusion mass transfer in gaseous phase to thermal conductivity of refractories," Inzh.-Fiz. Zh., 34, 452-455 (1978).
2. T. M. Muratova, "Kinetic theory of linear evaporation and condensation processes," Author's Abstract of Candidate's Dissertation, Moscow (1970).
3. K. Katayama, Y. Hayashi, and T. Kimura, "Researches on heat and mass transfer by sublimation of ice," Trans. Japn. Soc. Mech. Eng., 34, No. 263, 1232-1238 (1968). See also: D. P. Lebedev and T. L. Perel'man, Heat and Mass Transfer in Sublimation Processes in a Vacuum [in Russian], Énergiya, Moscow (1973).
4. S. Dushman and J. M. Lafferty, Scientific Foundations of Vacuum Technique, Wiley (1962).

5. M. N. Ivanovskii, V. P. Sorokin, and V. I. Subbotin, Evaporation and Condensation of Metals [in Russian], Atomizdat, Moscow (1976).
6. S. Bretshainder, Properties of Gases and Liquids [in Russian], Khimiya, Moscow—Leningrad (1966).
7. V. V. Pustovalov, Thermal Conductivity of Refractories [in Russian], Metallurgiya, Moscow (1966).
8. E. Ya. Litovskii, Ya. A. Landa, and I. D. Zborovskii, "Study of thermal conductivity of refractory materials over wide temperature range in a rarefied gas medium," Teplofiz. Vys. Temp., 15, 615-621 (1977).
9. E. Ya. Litovskii, Ya. A. Landa, and N. A. Puchkelevich, "Thermophysical properties of refractories upon rarefaction of the gaseous medium," Ogneupory, No. 1, 13-18 (1977).

EQUILIBRIUM SPEED OF SOUND IN A DISSOCIATING GAS

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An expression is obtained for the speed of sound in dissociating nitrogen tetroxide with consideration of the nonideality of the gas.

Dissociating nitrogen tetroxide shows promise as a heat-exchange agent and working substance in nuclear energy equipment.

To derive an expression for the equilibrium speed of sound in this system (gas), we will use the formula

$$a=\sqrt{\left(\frac{\partial p}{\partial \rho}\right)_s}, \tag{1}$$

where s indicates isentropic conditions. Expressing a in terms of the specific volume, we obtain

$$a^2=-v^2\left(\frac{\partial p}{\partial v}\right)_s. \tag{2}$$

For the partial derivative in Eq. (2) we will use the formula [1]

$$\left(\frac{\partial p}{\partial v}\right)_s=-\frac{C_p}{C_v}\frac{\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial v}{\partial T}\right)_p}. \tag{3}$$

There is a relationship between the partial derivatives of the function of two independent variables:

$$\left(\frac{\partial v}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial T}{\partial v}\right)_p=-1. \tag{4}$$

Defining $(\partial p/\partial T)_V$ from this expression and substituting in Eq. (3), we obtain

$$\left(\frac{\partial p}{\partial v}\right)_s=\frac{C_p}{C_v}\frac{\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial v}{\partial p}\right)_T}. \tag{5}$$

We will now use the differential equation [1]

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