

# CONTRIBUTION OF SEGREGATION AND DIFFUSION TO REFRACTORY-MATERIAL HEAT CONDUCTION

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The relation of segregation and diffusion in the solid phase with refractory-material heat conduction is shown.\*

Experimental investigation shows that on attenuation of the gaseous medium the thermal conductivity [1, 2] and thermal diffusivity [3] of dense and compressed refractory materials increase with rise in the air temperature. In [4-6] this rise is attributed to the intensification of heat and mass transfer through the gas phase with heterogeneous physicochemical transformations (vaporization, chemical transformation, etc.). However, as was noted in [4-6], this mechanism may only operate for any considerable time in thin (semiclosed) pores and microcracks, from which the escape of gaseous products is difficult, and in which the pressure is close to equilibrium. In addition, only a few components of refractory materials - mainly impurities - are able to develop an equilibrium pressure (0.1-1 torr) at temperatures of the order of 1000°K, and thereby to ensure that the processes are sufficiently rapid. There is therefore a need for further investigation of heat and mass transfer in refractory materials, in particular when no gaseous products are formed.

The present work continues the analysis of heterogeneous (heterophase) processes in refractory materials in the field of a temperature gradient. In particular, the relation of segregation and diffusion to the grain boundaries with the change in effective heat conduction of the material is demonstrated.

As a preliminary, to establish the basis of the proposed model, some results on segregation and diffusion in porous materials will be briefly considered.

It is known that the impurity concentration in regions adjacent to the pore surfaces and the grain boundaries of polycrystalline materials often exceeds the bulk impurity concentration. This effect is usually known as segregation. An up-to-date review of segregation and associated processes in polycrystalline materials may be found in [7] and for ceramic oxides in [8]. Segregation in ceramics is generally understood to include the following forms of change of state: increase or decrease in the concentration of lattice defects or dissolved material close to an internal boundary, adsorption of atoms of dissolved material at such a boundary, the appearance of new phase between the grains (the formation of films and particles along a boundary). It has been shown in many works that even when the total amount of impurity is very small, segregation may be very considerable. The following is a typical example [9]. High-purity samples of polycrystalline magnesium oxide were investigated using an electronic microprobe. At a bulk Si concentration of 55 ppm (determined mass-spectroscopically), the Si concentration of the grain boundary, recalculated as SiO<sub>2</sub>, reached 22 wt.%. In [8], in particular, it was maintained that at present there is no oxide ceramic in which segregated impurity is absent; even in the so-called "very pure" materials the fraction of the surface occupied by impurities (i.e., covered by at least a monolayer) is to be measured in tens of percent.

Thermodynamic analysis of segregation [7, 8, 10] shown that the transfer of impurity from the volume to the surface and in the opposite direction is accompanied by a definite energy expenditure  $\Delta Q$  (on the order of 10-50 kcal/mole). The equilibrium concentration of segregated material  $\rho(T)$  may be described in the first approximation by the relation

$$\rho(T) = \rho_0 \exp(\Delta Q/RT). \quad (1)$$

Here T is the temperature and R the universal gas constant.

Thus, when the sample contains a temperature gradient, there is a difference in the concentration of segregated material at the "hot" and "cold" walls of pores and microcracks and, correspondingly, a mass flux

\*The basic calculation scheme was proposed by E. Ya. Litovskii.

TABLE 1. Calculated Values of  $\lambda^E$ , W/10<sup>-3</sup> deg K

d, m	D, cm <sup>2</sup> /sec			
	10 <sup>-5</sup>	10 <sup>-7</sup>	10 <sup>-6</sup>	10 <sup>-4</sup>
10 <sup>-8</sup>	2,1·10 <sup>-5</sup>	2,1·10 <sup>-4</sup>	2,1·10 <sup>-3</sup>	2,1·10 <sup>-2</sup>
10 <sup>-7</sup>	2,1·10 <sup>-6</sup>	2,1·10 <sup>-5</sup>	2,1·10 <sup>-4</sup>	2,1·10 <sup>-3</sup>
10 <sup>-6</sup>	2,1·10 <sup>-7</sup>	2,1·10 <sup>-6</sup>	2,1·10 <sup>-5</sup>	2,1·10 <sup>-4</sup>

by surface diffusion. If the rate at which equilibrium concentrations are established is sufficiently high, the mass flux will be directed from the volume to the surface at one side of the pore and from the surface to the volume at the opposite side. A heat transfer through the pore corresponding to this flux is evidently caused by the change in its effective heat conduction.

Note that the concentration difference at the surface and the mass flux due to surface diffusion cause a shift in the bulk equilibrium concentration and hence mass transfer in the opposite direction in the deeper layers and in the grain volume. Adopting the model of the elementary stages of heterogeneous processes developed in [11], it may be assumed that both mass fluxes are localized in the surface layer. The resulting mass flux in the material depends on the ratio between these fluxes [10], but the effective heat transfer remains in all cases.

To estimate the size of this effect, consider a pore model in the form of a finite cylinder of diameter  $d$  and height  $\delta$ . The plane parallel ends of the cylinder are at temperatures  $T_1$  and  $T_2$ ; to be specific, let  $T_1 > T_2$ . The temperature distribution along the generatrix of the pore is linear. Assume further that an impurity is segregated in the surface layer of the pore, of thickness  $h$ ; the impurity concentrations at the plane ends of the pore correspond to Eq. (1), and are  $\rho(T_1)$  and  $\rho(T_2)$ . The mass flux over the side surface of the cylinder is

$$j = D \frac{\rho(T_1) - \rho(T_2)}{\delta} \pi d h. \quad (2)$$

Here  $D$  is the surface-diffusion coefficient.

Substituting the values of  $\rho_1$  and  $\rho_2$  into Eq. (2), and taking into account that  $\Delta Q \Delta T / RT^2 \ll 1$ , where  $\Delta T = T_1 - T_2$ ,  $T = (T_1 T_2)^{1/2}$ , the following result is obtained

$$j = D \frac{\pi d h}{\delta} \rho(T) \frac{\Delta Q \Delta T}{RT^2}. \quad (3)$$

The effective heat transfer through the pore is

$$q = j \Delta Q = D \frac{\pi d h}{\delta} \rho(T) \frac{(\Delta Q)^2 \Delta T}{RT^2}. \quad (4)$$

Defining the associated component of the pore heat conduction as

$$\lambda^E = \frac{q}{\Delta T} \cdot \frac{4\delta}{\pi d^2}, \quad (5)$$

it follows that

$$\lambda^E = D \rho(T) \frac{(\Delta Q)^2}{RT^2} \cdot \frac{4h}{d}. \quad (6)$$

Note at once that this expression has been derived on the basis of a very coarse schematization of a complex process. In particular, the concepts developed in [7, 8, 10] may be used to refine the diffusional-flux paths, to distinguish between diffusional motive forces, to take into account the nonequilibrium features of the process and the specific features of the individual diffusion mechanisms, etc. However, this leads to considerable complication of the calculations and, above all, to the appearance of new parameters which are not easy to determine. Accordingly, a first estimate will be made using Eq. (6).

As a preliminary, the order of the absolute heat conduction ( $\lambda^{\delta}$ ) of microcracks (or pores) at a grain boundary is determined; this is necessary for the interpretation of experimental data on the effective heat conduction of the material ( $\lambda_{\text{eff}}$ ). Suppose that the effective contact area between particles at grain boundaries ( $\bar{a}^2$ ) is 1-5% of the grain cross-sectional area, while the microcrack (boundary) thickness  $\bar{\delta}$  is 0.1-1% of

the particle diameter. This order of magnitude follows from boundary-structure investigations in polycrystalline materials [7, 12], and allows the change in  $\lambda_{\text{eff}}$  in various gaseous media to be explained [13, 14]. With the given parameters it may readily be shown, using the equations proposed in [13], that the value of  $\lambda^{\delta}$  must be  $5 \cdot 10^{-5} - 10^{-3} \text{ W/10}^{-3} \text{ }^{\circ}\text{K}$  in order to ensure the experimentally observed heat-conduction values of polycrystalline refractory oxides at  $T = 1000^{\circ}\text{K}$ .

The parameters in Eq. (6) will now be estimated. In accordance with [7, 8], suppose that  $\Delta Q = 20 \text{ kcal/mole}$ ; let  $M = 16 \text{ g/mole}$ ,  $\rho = 10^6 \text{ g/m}^3$ ,  $h = 10^{-9} \text{ m}$ , and  $T = 1000^{\circ}\text{K}$ . The surface-diffusion coefficient of various elements is  $10^{-9} - 10^{-7} \text{ cm}^2/\text{sec}$  in polycrystals and  $10^{-7} - 10^{-5} \text{ cm}^2/\text{sec}$  in vitreous phase [7, 8]. It is suggested in [15] that the boundary structure of ceramic materials and, correspondingly, the diffusion coefficient correspond more closely to data on the vitreous phase. Since a highly irregular boundary may be regarded as an ultra-pore structure [7, 12, 15],  $d$  may vary over the range  $10^{-8} - 10^{-6} \text{ m}$ . Values of  $\lambda^E$  calculated for different values of  $D$  and  $d$  are shown in Table 1. It is evident from Table 1 that for the given parameter values  $\lambda^E$  takes values of  $10^{-5} - 10^{-3} \text{ W/10}^{-3} \text{ deg K}$  in ultrapores, i.e., makes a marked contribution to the effective heat conduction of the material. With decrease in temperature, the diffusion coefficient falls sharply (as an exponential with a large exponent) and, correspondingly, so does  $\lambda^E$ , which also agrees with experimental data on the effective heat conduction of refractory materials on attenuation of the gaseous medium. In view of the limited rate of diffusional mass transfer in the model adopted, the contribution of the given mechanism to the effective heat conduction of macropores is negligibly small.

#### LITERATURE CITED

1. V. V. Pustovalov, Heat Conduction of Refractory Materials [in Russian], Metallurgiya, Moscow (1966).
2. E. Ya. Litovskii, Ya. A. Landa, and I. L. Zborovskii, Teplofiz. Vys. Temp., No. 3 (1971).
3. E. Ya. Litovskii, N. A. Puchkelevich, and Ya. A. Landa, Ogneupory, No. 1 (1977).
4. E. Ya. Litovskii, F. S. Kaplan, and A. V. Klimovich, Teplofiz. Vys. Temp., No. 4 (1977).
5. E. Ya. Litovskii, F. S. Kaplan, and A. V. Klimovich, Inzh. -Fiz. Zh., 33, No. 1, 101 (1977).
6. E. Ya. Litovskii, F. S. Kaplan, and A. V. Klimovich, Inzh. -Fiz. Zh., 34, No. 3, 452 (1978).
7. G. Gleiter and B. Chalmers, Highly Irregular Grain Boundaries [Russian translation], Mir, Moscow (1975).
8. W. D. Kingery, J. A. C. S., 57, No. 2, 74-83 (1974).
9. M. H. Leipold, Ceramic Microstructures, Wiley, New York (1968), p. 289.
10. Ya. E. Geguzin and M. A. Krivoglaz, Motion of Macroscopic Inclusions in Solids [in Russian], Metallurgiya, Moscow (1971).
11. P. Barre, Kinetics of Heterogeneous Processes [Russian translation], Mir, Moscow (1975).
12. W. D. Kingery, J. A. C. S., 57, No. 1, 1-8 (1974).
13. G. N. Dul'nev, Yu. P. Zarichnyak, and E. Ya. Litovskii, "Model for the calculation of ceramic heat conduction," in: Thermophysical Properties of Solids. Materials of the Third All-Union Thermophysical Conference on the High-Temperature Properties of Materials, Baku, 1968 [in Russian], Naukova Dumka, Kiev (1971), p. 76.
14. T. V. Sokolova, E. Ya. Litovskii, and T. B. Buzovkina, Izv. Akad. Nauk SSSR, Ser. Neorg. Mater., 9, No. 2 (1973).
15. W. D. Kingery, Introduction to Ceramics, Wiley, New York (1976).