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CONTRIBUTION OF CRYSTALLINE LATTICE DEFECTS TO THERMAL CONDUCTIVITY OF POROUS MATERIALS

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UDC 536.21

The relationship of pore thermal resistance and effective thermal conductivity of porous media to the processes of crystalline lattice defect formation and motion is demonstrated.

The effect of lattice defects on the thermal conductivity of crystalline solids is widely known [1, 2]. However, the dependence of thermal resistance of pores and intergrain boundaries in porous media on this factor has been studied insufficiently. At the same time, the thermophysical properties of porous oxide systems depend decisively on the intensity of heat transfer between grains.

A number of studies [3-6] have analyzed the temperature dependence of thermal conductivity of such systems in rarefied gaseous media. In particular, the possibility of reversible change in the interparticle contact spot under the action of thermal stresses has been noted [3]. The effects of change in gas pressure within pores [4], and heat–mass transfer with participation of both the gaseous [5] and solid [6] phases have been considered. However, these mechanisms cannot satisfactorily explain the available experimental data, according to which, e.g., [7], the thermal conductivity of high-purity (99.99%) yttrium oxides in a vacuum obeys the same laws as do technological-grade refractories, remaining stable for long time periods. Results of experiments with especially pure oxides compel assumption of the existence of a heat–mass transfer mechanism within polycrystalline porous materials related to development and motion of crystalline lattice defects within the temperature gradient field near the surface of pores and microcracks.

The effect of such processes can be analyzed conveniently using the "quasichemical approach" of Wagner, Crager, and Wink [8], with the aid of which the crystal-structure defect concentration can be determined for a given temperature and gaseous medium composition. In the presence of a temperature gradient within the pores and microcracks, the change in the equilibrium constant K of the defect formation process follows a law

$$K = A\exp(\Delta S^0/k)\exp(-\Delta H^0/kT). \tag{1}$$

All-Union Refractory Institute, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 44, No. 6, pp. 965-969, June, 1983. Original article submitted February 15, 1982.

0022-0841/83/4406-0657$07.50

This in turn leads to development of a concentration gradient and diffusion flow. Knowing the latter, and using the expressions presented in [5, 6], one can calculate the thermal conductivity component λ_E within the pores, and then the effective thermal conductivity of the material [9].

For Y_2O_3-type oxide systems the most significant processes are apparently formation of oxygen vacancies and their ionization [10]:

$$O \xrightleftharpoons{K_1(T)} O_o^{\times} + V_o^{\times} \xrightleftharpoons{K_2(T)} O_i' + V_o^{\cdot} \xrightleftharpoons{K_3(T)} O_i'' + V_o^{\cdot\cdot}. \qquad (2)$$

It is evident from the reaction equations that in the presence of a temperature gradient a shift in equilibrium occurs ($K(T_1) \neq K(T_2)$). This leads to differing reaction-product concentrations on the pore walls, and thus to development of diffusion heat—mass transfer along the walls, i.e., to shunting of the thermal resistance of pores, microcracks, and intergrain boundaries.

Analysis reveals that for insignificant defect concentrations, the principles of defect diffusion in the temperature gradient field will be analogous to those found for heat—mass exchange in chemically reacting gas mixtures (a "defect gas"). Moreover, the mutual diffusion coefficient for materials with composition close to stoichiometric proves to be significantly higher than the anion or cation diffusion coefficient [10]. Calculations of the thermal conductivity of a porous ceramic with consideration of the above reveal that the mechanism considered is sufficient to shunt the thermal resistance of pores 0.1-1 μm in diameter.

We will illustrate this with a concrete example, using the expression for the effective thermal conductivity of a cylindrical pore obtained by the present authors previously in an analysis of segregation and diffusion processes [6]:

$$\lambda_E = D_s C \frac{(\Delta Q)^2}{RT^2} \frac{4h}{d}, \ \mathrm{W/m\cdot{}^\circ K}. \qquad (3)$$

We will perform calculations for the example of yttrium oxide — a typical nonstoichiometric compound, which easily forms oxygen-deficient compositions of the type Y_2O_{3-x}. Contemporary thought characterizes the structure of such compounds by anti-Frankel type disordering with dominance of one type of defect—anion vacancies [10-12].

For the oxygen diffusion coefficient through anion vacancies in Y_2O_3 we have [13]: $D_V = D_{Vo}\exp(-Q_{act}/kT)$, $D_{Vo} = 6.06\cdot10^{-6}$ cm²/sec, $Q_{act} = 0.85$ eV; here $Q_{act} = \Delta H_m$ is the oxygen-ion energy through vacancies of its own sublattice. According to [11, 14-16], $D_S = (10^5-10^{11})D_V$. Choosing for calculation $D_S = 10^8 D_V$, we obtain $D_S = 6.06\cdot10^{-2}\exp(-9855/T)$, m²/sec.

We will now estimate the defect concentration in Y_2O_{3-x}. Since in the present case one type of defect predominates, its concentration [N] is related to the quantity x by the expression $[N] = x\rho N_A/M$, m^{-3} ($\rho_{theo} = 5.03\cdot10^3$ kg/m³, $M_{Y_2O_3} = 2.26\cdot10^{-1}$ kg/mole). For Y_2O_{3-x} the value $x = (1-2)\cdot10^{-2}$ is reached easily [10, 11]. Thus, if, allowing a margin for error, we choose $x = (1-10)\cdot10^{-3}$ at 1000°C, we have $[N] = 1.3\cdot(10^{25}-10^{26})$ m^{-3}, i.e., $C = [N]/N_A = 2.2\cdot(10^1-10^2)$ mole/m³.

In the present case the thermal effect of the process is related to the enthalpy of oxygen vacancy formation $\Delta H_{V_O^{\cdot\cdot}}$. According to [11], the activation energy for self-diffusion and electrical conductivity for transfer through anion vacancies in oxides with an oxygen deficit is $E_{act} = \Delta H_{V_O^{\cdot\cdot}}/3 + \Delta H_m$. Electrical conductivity measurements of Y_2O_3 give $E_{act} \approx 1.9$ eV [17-19]. The migration energy $\Delta H_m \approx 0.85$ eV [13]. Thus, $\Delta H_{V_O^{\cdot\cdot}} = 3.15$ eV (≈73 kcal/mole). The value of ΔQ in Eq. (3) is obtained from the temperature dependence of concentration, and since in the given case $C \sim \exp(-\Delta H_{V_O^{\cdot\cdot}}/3kT)$ [11], we obtain $\Delta Q = \Delta H_{V_O^{\cdot\cdot}}/3 = 1.05$ eV.

We will evaluate the geometric parameters. We take h = 10 Å = 10^{-9} m. This is the minimum value of the thickness of the layer in which surface diffusion occurs in the ideal case [15]. Such an estimate is very low; according to [14-16], surface and grain boundary diffusion can actually occur in much thicker (up to 100 Å) layers. Finally, we take d = 0.1 μm = 10^{-7} m. This was the typical size of pores at intergrain boundaries in our specimens, as determined by mercury porometry and electron microphotographs [7].

Thus, we have the following initial data for calculation: T = 1273°K, $D_S = 6.06\cdot10^{-2}\cdot\exp(-9855/1273) = 2.63\cdot10^{-5}$ m²/sec, $C = 2.2\cdot(10^1-10^2)$ mole/m³, $\Delta Q = 1.05$ eV = 10^5 J/mole, h =

10^{-9} m, $d = 10^{-7}$ m. Substituting these parameters in Eq. (3), we finally obtain $\lambda_E = 1.7 \cdot (10^{-2}-10^{-1})$ W/m·deg K, which is comparable to the thermal conductivity of pores filled with gas at normal pressure. We must note the important advantages of the proposed heat–mass transfer mechanism in comparison to those considered earlier [4-6]:

1) the presence of structural defects is characteristic of all oxide systems, so that the given mechanism for reduction of pore thermal resistance is realized upon heating in vacuo of both industrial and special purity refractory oxides;

2) in contrast to the previously proposed process of diffusion of segregated impurities, in the present mechanism the entire process can be localized in a surface layer, and the low values of the volume diffusion coefficient do not limit the intensity of heat–mass transfer;

3) the thermal effect of the process of defect formation, in particular, oxygen vacancy formation, is higher than that of the segregation process [6, 8], and with consideration of the fact that $\lambda_E \sim (\Delta Q)^2$, its realization will lead to more intense heat transfer at high temperatures.

To refine the type of defect involved and the concentration of those defects, the full array of contemporary experimental techniques can be used: measurements of thermo-emf, electrical conductivity, thermogravimetry, electron paramagnetic resonance, isotope methods, etc. [8, 10-12].

In conclusion, we note that in both industrial refractories and high purity porous materials, the contribution to thermal conductivity of solid-phase chemical reactions occurring without formation of gaseous products, of solid solution formation, etc., can be treated in a similar manner.

NOTATION

ΔS°, ΔH°, entropy and enthalpy related to formation of crystalline lattice defects in bodies or their complexes; 0, notation for defect-free crystal; $O_o^\times$, oxygen atom at its proper place in the lattice; O_i', O_i'', oxygen anions in interstices with effective charges of −1 and −2; $V_O^\times$, $V_O^\cdot$, V_O, oxygen vacancies in anion sublattice with zero, positive, and double positive charges; D_v, D_s, volume and surface diffusion coefficients; C and [N], molar and numerical concentrations; ΔQ, effective heat of process; d, pore diameter; h, thickness of diffusion layer; ρ, specimen density; M, molecular mass of compound; N_A, Avogadro's number.

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EFFECTIVE THERMAL EXPANSION COEFFICIENT IN A NONUNIFORM MATERIAL

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UDC 539.3

Lower and upper bounds are determined for the thermal expansion coefficient in a nonuniform material.

Statement of the Problem. In determining the effective properties of a nonuniform material, one normally transforms the nonuniform medium to quasihomogeneous one having the required properties. The necessary and sufficient condition that this approach be valid is that the characteristic size of the nonuniformities l satisfy the inequality

$$l_0 \ll l \ll L, \tag{1}$$

where l_0 is the linear dimension of an elementary cell in the crystal lattice, and L is the dimension of the sample of nonuniform material.

The effective thermal expansion coefficient tensor, in the case of a quasihomogeneous medium, is given by

$$\langle \varepsilon_{ij} \rangle = \alpha_{ij}\Delta T, \tag{2}$$

where $\Delta T = T - T_0$, with T_0 the initial and T the final temperature of the medium. $\langle \varepsilon_{ij} \rangle$ is the deformation tensor averaged over the volume $V \sim L^3$ of the sample:

$$\langle \varepsilon_{ij} \rangle = \frac{1}{V} \iiint\limits_V \varepsilon_{ij}(\mathbf{r})\, d^3\mathbf{r}. \tag{3}$$

Locally the following relations are valid:

$$\varepsilon_{ij}(\mathbf{r}) = S_{ijkl}(\mathbf{r})\,\sigma_{kl}(\mathbf{r}) + \alpha_{ij}(\mathbf{r})\,\Delta T, \tag{4}$$

Moscow Institute of Chemical Engineering. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 44, No. 6, pp. 969-977, June, 1983. Original article submitted January 2, 1982.

0022-0841/83/4406-0660$07.50