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Effect of surface segregation kinetics on the effective thermal conductivity of porous ceramics

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Abstract—Thermophysical properties of some porous refractory materials depend upon the thermal history of the samples tested. Sometimes repetitive measurements of thermal conductivity, performed at constant thermodynamic conditions, yield results that continue to change during tens of hours after a thermal equilibrium seems to be established. This phenomenon is shown to be attributable to a redistribution of impurities (normally present in all industrial ceramics) in the vicinity of pores existing in the grain boundary region, separating poorly sintered granules. This mass redistribution process is induced by changes of the material temperature. Its rate is shown to be governed by diffusion of impurities to and from the pores. This process in refractory ceramics is very slow (i.e. occurs on the time scale of tens of hours), which incurs the concomitant slow changes of the effective thermal conductivity. A physico-mathematical model of the surface segregation kinetics is developed. Relative influences of the pore sizes and the segregation kinetic parameters on the mass redistribution rate and surface concentration of impurities are analyzed. These results are further used to calculate the temporal variation of the effective thermal conductivity, resulting from an instantaneous change of the material temperature. The results are shown to agree with experimental data collected for porous yttrium oxide ceramic material. The model developed here can be used to explain and rationalize the dependence of thermal conductivity on the material thermal history and the measurement method.

1. INTRODUCTION

Thermal conductivity (k) and diffusivity (a) of porous ceramic materials are important properties required in numerous engineering applications [1]. Much scientific and engineering effort has been devoted to measurements and calculations of these quantities for ceramic and refractory materials in various thermodynamic conditions. These conditions, especially temperature and gas pressure, are dictated by the specific applications and the materials' operating conditions. They may vary from atmospheric conditions ($p = 1$ atm, $T = 300$ K) to high temperatures (about 2300 K [1]) and low pressures (about 10^{-5} Pa [1]).

Measurements of thermophysical properties are widely performed at various stages of design of ceramic materials, construction of thermal aggregates and during control of existing equipment. Development of reliable methods for measurement of k and a is an important metrological problem, which requires proper characterization of the material chemical composition and structure, and understanding of heat transfer mechanisms in porous composite materials.

Thermal behavior of volumetrically uniform, chemically clean materials, for example, of metal oxides, is well documented [2]. However, various requirements (e.g. imposed on the material strength, thermal shock resistance, tribological properties, etc.) result in fabrication of ceramic materials characterized by complicated chemical compositions and microstructure. Thermophysical properties of these materials often change with temperature and gas pressure in a manner which is difficult to understand and rationalize on the basis of the classical theory of conduction, convection and radiation heat transfer in porous and composite materials [3, 4]. Moreover, k and a of industrial ceramics and refractories sometimes depend on the thermal history of the samples tested. In particular, thermal conductivities of some materials measured in low gas pressure, change during a long time (tens of hours) after thermal equilibrium is established. Such experimental data for Y_2O_3 are shown in Fig. 1. The sample, initially maintained at temperature 1400°C, was instantaneously put into a chamber with temperature 600°C. After that, its thermal conductivity, measured every 15 min, appeared to rise monotonously during the first 20 h of experiment, which is much longer than the time needed for establishment of a steady temperature field [5]. This paper is aimed at providing a physical explanation and a mathematical model for such a behavior of thermophysical properties of industrial ceramic and refractory materials.

Heat transfer in porous ceramics is governed by several mechanisms, which include conduction in the solid phase and in pores, thermal radiation and gas

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NOMENCLATURE

a	thermal diffusivity
a_{bs}	thermal diffusivity of the solid phase
b	average distance between the pores forming pore chain
C	molar fraction of impurities in the bulk solid phase
C_s	molar fraction of impurities on pore surfaces
d	pore diameter
$\bar{d}$	dimensionless pore diameter defined in equation (15)
D	volumetric diffusivity of impurities
D_s	diffusivity of impurities on pore surfaces
f	function accounting for the limiting role of bulk diffusion on pore phase conductivity
F	function relating bulk and surface concentration of impurities
H	size of a sample
k	thermal conductivity
k_{eff}	effective thermal conductivity
k_g	thermal conductivity of gas filling pores
k_p	pore phase conductivity
k_{SD}	pore phase conductivity component associated with segregation–diffusion
K	surface segregation kinetic coefficient
L	grain size
M	function determining the influence of heat barrier resistances on the effective thermal conductivity
M	molar mass of the solid phase
p	pressure
Q	segregation specific enthalpy
r	radial coordinate
s	Laplace's variable
t	time variable
T	temperature.

Greek symbols

α_C	coefficient defined in equation (14)
δ	thickness of the surface layer
ε	material porosity (void fraction)
μ	segregation Damköhler number defined in equation (16)
ρ	density of the solid phase
τ	dimensionless time variable, defined in equation (18)
τ_H	time, required for establishing a steady temperature field
$\tau_{C,L}$	time scale of redistribution of impurities within the grain
$\tau_{T,L}$	time scale associated with heat diffusion within the grain
ψ	function reciprocal to F.

Subscripts

∞	value far from the pore
s	value on pore surface
bs	bulk solid phase
p	pore
SD	segregation–diffusion
g	gas
eff	effective property
1	initial state
2	final state.

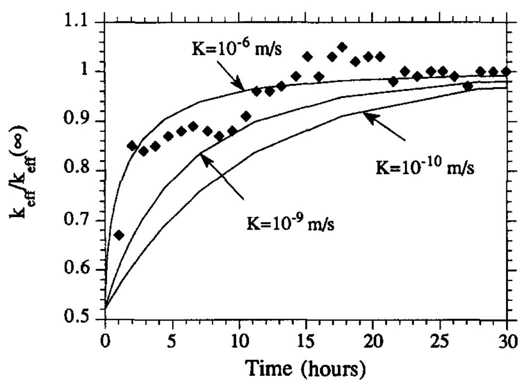

Fig. 1. Temporal dependence of effective thermal conductivity of porous Y_2O_3 ceramic material in vacuum after its temperature was changed from 1400 to 600°C. Experimental data are from ref. [5]. Theoretical curves: k_{eff} is calculated via equations (21) and (22); C_s is obtained by inverting equation (17); $d = 1$ μm, $D = 10^{-15}$ m^2 s^{-1}.

convective motion in pores [5]. The last two mechanisms are ineffective in dense ceramic materials with small pores [5], where the effective (apparent) thermophysical properties (k_{eff}, a_{eff}) appear to be determined by heat conduction only.

Various models for the effective thermal conductivity of composite materials have been developed [6–11]. Approximate geometrical models [6, 11] and more rigorous homogenization methods [8–10] focused on relatively large-scale effects of geometry and size of particles composing the material. These methods were proven useful in predicting thermophysical properties of highly porous materials (e.g. insulations). However they are inapplicable for dense ceramic materials which contain cracks, pores and other inhomogeneities of different sizes, ranging from microcracks of nano- and micrometer size to large pores of several millimeters. Samples which appear macroscopically homogeneous may contain small amounts of pores in the regions separating poorly sintered granules (grain boundary regions [1]). Chains of these pores and the associated heat barrier resistances were shown to dramatically affect the pressure and temperature dependences of the material thermophysical properties [5].

In our recent contribution [12] we showed that the effective thermal conductivity of dense ceramic materials in vacuum is significantly affected by motion of impurities in the vicinity of pores. These impurities may be admixtures added as chemically binding substances during material fabrication, or defects of the material crystal lattice structure. Diffusion of miniscule amounts of these impurities and their segregation on pore surfaces are accompanied by heat transfer across pores. This process constitutes a mechanism which in vacuum controls the material effective thermal conductivity [5].

In this paper we go beyond the steady state analyses performed in ref. [12] and investigate kinetics of the segregation–diffusion process. The unsteady mass transfer analysis is incorporated to explain the effect of the material thermal history on time-dependence of the effective thermal conductivity at low pressures. Explicitly, we attribute this hysteresis phenomenon to a redistribution of impurities near pores, caused by changing material temperature. This redistribution is controlled by a diffusion of impurities in grains and grain boundary regions, which is a very slow process [13], especially at low temperatures. A physico-mathematical model developed here allows us to establish the evolution of concentration of impurities on pore surfaces and to calculate the concomitant evolution of the effective thermal conductivity. The importance of the results obtained here is discussed in relation to laboratory measurements of the material thermophysical properties *viz-à-viz* known standard methods.

2. PHYSICAL MODEL

Measurements of the thermal conductivity of ceramic samples may be performed by several methods, which can be subdivided into stationary and nonstationary ones [14, 15]. In stationary methods, a sample to be tested is held in a steady temperature field for a sufficiently long time to ensure that all transient heat fluxes vanish. Measurement of thermal conductivity is then performed under steady-state conditions where local thermodynamic equilibrium may be assumed to prevail in every point of the sample.

The materials considered here are assumed to be composed of sintered grains (of typical size of 50–100 μm) and to contain small pores (of sizes 0.1–1 μm) located in the grain boundary region (see Fig. 2). Furthermore, these materials are supposed to contain a certain (usually small) amount of impurities. These may be transported by diffusion, characterized by volumetric diffusivity D and segregate on surfaces of pores within the material.

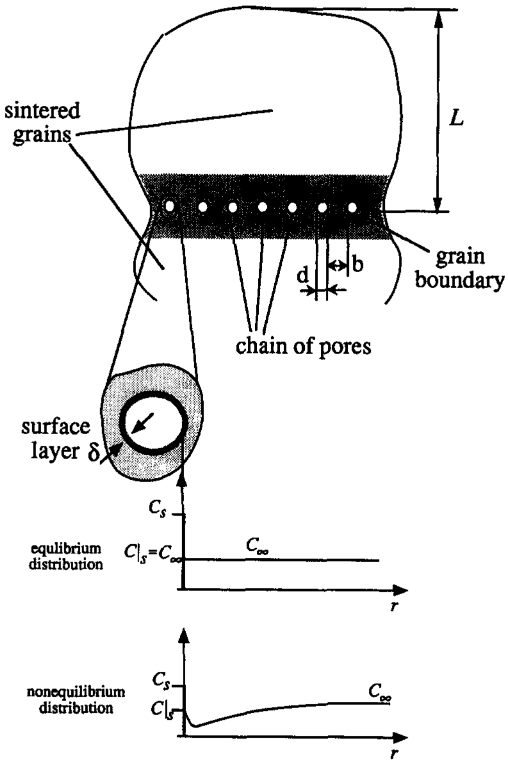

Fig. 2. Porous grain boundary of ceramic material.

Suppose that a sample of a size H to be tested is held during a long time in an environment (e.g. storage), where a constant temperature, say T_1, prevails. It is then placed in a furnace, where thermal conductivity measurement is to be performed at a certain average temperature, say T_2. The sample is held within the furnace (prior to taking measurement) under a specified temperature gradient during a time τ_H, required for establishing a steady temperature field. This time is usually estimated as

$$\tau_H > H^2/a, \qquad (1)$$

where a is the (effective) material thermal diffusivity at temperature T_2. For a typical sample of $H \sim 0.05$ m with $a \sim 10^{-4}$ m^2 s^{-1}τ_H is of order of 1 h. This time is usually required in stationary methods as a necessary exposure time, after which thermal conductivity is measured.

Although macroscopically, at $t > \tau_H$ the sample appears to be in a steady state, in the microscopic sense local thermal equilibrium may not exist. Indeed, in equilibrium conditions corresponding to temperature T_1 the constant concentrations of impurities in the bulk, C_∞, and on the surface, C_s, are related by a segregation isotherm [1, 16]

$$C_s = C_{s1} = F(C_\infty, T_1). \qquad (2)$$

The equilibrium surface concentration C_{s1}, given by equation (2) is, however, not consistent with the new material temperature T_2. As a result, the impurities are set in motion towards a new equilibrium value of the surface concentration :[†]

$$C_{s2} = F(C_\infty, T_2). \qquad (3)$$

This microscopic grain-level process of redistribution of impurities near pores, induced by temperature changes, occurs on the time scale $\tau_{C,L}$ which is much larger than τ_H, as estimated above. To show this we will calculate $\tau_{C,L}$ using a characteristic grain size $L \approx 50$ μm and the data on bulk diffusivity of impurities $D = 10^{-15}-10^{-14}$ m^2 s^{-1} [17, 18]. This yields

$$\tau_{C,L} > \frac{L^2}{D} = 2.5 \cdot 10^5 - 2.5 \cdot 10^6 \text{ s} \qquad (4)$$

which is the time period ranging from tens to hundreds of h.

Comparison of relations (1) and (4) illustrates the large difference between the rates of macroscale heat transfer and microscale mass transfer processes. This means that after a relatively short time τ_H the mass transfer process in the sample may be viewed as occurring in a steady temperature field around T_2.

One should note that in spite of the apparent 'coarse-scale' steady temperature field that prevails within the sample at times $t > \tau_H$, the microscopic temperature field actually is not steady. If, for example, $T_2 > T_1$, the surface concentration decreases with time and excessive impurities migrate through the grain boundary and diffuse into the bulk. This process results in heat adsorption. Conversely, when $T_2 < T_1$, C_s tends to increase, and the impurities required at the surface are drawn from the bulk, which results in heat release.

The time scale associated with diffusion of heat, induced by these pore-level mass transfer processes and the concomitant temperature changes is

$$\tau_{T,L} > \frac{L^2}{a_{bs}}, \qquad (5)$$

where a_{bs} is the solid-phase thermal diffusivity at T_2. Evaluation of the above shows that $\tau_{T,L} \sim 0.025$ s, which means that the small amounts of heat generated (or adsorbed) in the vicinity of pores as a result of local mass redistribution, diffuse sufficiently fast, i.e.

$$\tau_{T,L} \ll \tau_H \ll \tau_{C,L}.$$

Thermal conductivity measurements performed by a stationary method require the application of a temperature gradient to the sample. However, for the purpose of evaluating the effect of the kinetics of the pore-level segregation–diffusion processes on the effective thermal conductivity, the sample having initial constant temperature T_1 is brought to an environment with another *constant* temperature T_2. The above estimates imply that for the time $t \ll \tau_H$, the microscale unsteady mass transfer analyses may be performed for an effectively isothermal material at T_2. The mathematical model developed below describes redistribution of impurities induced by a change of the material temperature, which occurs on the time scale comparable to $\tau_{C,L}$, greatly exceeding τ_H. In order to facilitate the treatment it will be assumed that the temperature within the sample is uniform and equal to T_2 *beginning from* $t = 0$. Thereby, we disregard the mass redistribution occurring during the initial temperature equilibration time period τ_H.

3. REACTION-DIFFUSION MODEL OF SEGREGATION KINETICS

Consider a ceramic material, characterized by pore chains, existing in the grain boundary region (see Fig. 2). We will calculate the evolution of the concentration of impurities in the vicinity of an isolated spherical pore of diameter d, resulting from an instantaneous change of the sample temperature from T_1 to T_2, as assumed in the previous section. The volumetric concentration of the impurities in the bulk region is governed by the diffusion equation

$$\frac{\partial C}{\partial t} = D\nabla^2 C. \qquad (6)$$

The equation of mass conservation at the pore surface is

$$\delta \frac{dC_s}{dt} = D\frac{\partial C}{\partial r}, \qquad (7)$$

where δ is the thickness of the surface layer of the segregated material. These equations are to be solved subject to the following initial conditions :

$$C_s(0) = C_{s1} = F(C_\infty, T_1) \qquad (8)$$

$$C(0, r) = C_\infty \quad d/2 < r < \infty \qquad (9)$$

and the boundary condition

$$C(t, r)|_{r\to\infty} = C_\infty, \quad t > 0. \qquad (10)$$

To close the problem we will note that the rate of change of surface concentration is governed by a driving force of the segregation process, which is assumed to be the difference between the current value of the volumetric concentration adjacent to the surface, $C|_s$ (see Fig. 2) and the value of this quantity which would prevail in equilibrium with the current surface concentration $C_s(t)$

$$\delta \frac{dC_s}{dt} = K\{C|_s - \psi[C_s(t), T_2]\}. \qquad (11)$$

In the above, the constant coefficient K is the surface segregation kinetic coefficient, which can be estimated theoretically or determined from experiments, ψ is the

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[†] Changes in the value C_∞ of the impurities bulk concentration with temperature, resulting from changing the amount of segregated substance, are negligible. This may be shown by evaluating the total mass segregated on the pore surfaces, compared with the mass of impurities accumulated in the volume.

function reciprocal to F [see, equations (2) and (3)], i.e. $\psi[C_s(t), T_2]$ is the *volumetric* concentration of impurities in the vicinity of the pore surface, consistent with the current value $C_s(t)$ in equilibrium.

The problem posed by equations (6)–(11) is solved in the circumstances where the distance between the pores is sufficiently large. In this case a single pore analysis can be performed and the problem is characterized by spherical symmetry. Equations (6)–(11) constitute a well posed problem that can be easily generalized to account for any other pore geometry (e.g. cylindrical or ellipsoidal).

In order to simplify the solution we will linearize the C_s-dependence of ψ in the following form:

$$\psi(C_s, T_2) = C_\infty + \frac{C_s - C_{s2}}{\alpha_C} \tag{12}$$

where

$$C_{s2} = F(C_\infty, T_2) \tag{13}$$

and

$$\alpha_C = \left(\frac{\partial C_s}{\partial C}\right)\bigg|_{C_\infty, T_2}. \tag{14}$$

With this simplification, the problem contains the following dimensionless parameters:

$$\bar{d} = \frac{d}{\alpha_C \delta} \tag{15}$$

$$\mu = \frac{D}{\alpha_C K d}. \tag{16}$$

In the above, $\bar{d}$ characterizes the relative effect of the pore curvature. The limiting case $\bar{d} \to \infty$ describes the segregation kinetics on the surface of a homogeneous semi-infinite material, bounded by a plane boundary. The dimensionless complex μ represents the ratio of the characteristic segregation time scale to the diffusion time scale, and may be interpreted as the segregation Damköhler number. If $\mu \ll 1$, the diffusion time is much larger than the characteristic time of segregation, and the process is diffusion-controlled.

If $\mu \ll 1$, the characteristic segregation time exceeds the characteristic time of diffusion, and the process is controlled by the segregation kinetics.

Equations (6)–(11) were solved by Laplace transform method, with the solution in the s-domain being

$$\frac{C_s(\tau, \mu) - C_{s2}}{C_{s1} - C_{s2}} = 1 - \mathbf{L}^{-1}\left[\frac{1}{s\left(\mu s + \dfrac{\bar{d}s}{\bar{d}\sqrt{s}+2} + 1\right)}\right], \tag{17}$$

where s is the Laplace transform variable, and $\mathbf{L}^{-1}$ is the inverse transform operator, and τ is the dimensionless time variable defined by

$$\tau = \frac{tD}{\alpha_C^2 \delta^2}. \tag{18}$$

Details of the spatial distribution and temporal evolution of C can be found in ref. [19]. Here attention will be focused on the asymptotic behavior of the surface concentration of impurities, $C_s(t)$. It can be shown that for the short times ($\tau \ll \mu$ or $t \ll \alpha_C \delta / K$) the surface concentration behaves according to the exponential law

$$\frac{C_s - C_{s2}}{C_{s1} - C_{s2}} = \exp\left(-\frac{\tau}{\mu}\right) = \exp\left(-\frac{tK}{\alpha_C \delta}\right) \quad \tau \ll \mu, \tag{19}$$

which is typical for reaction-controlled segregation processes described by the Rawlings' model [20, 21]. It can be concluded that at the early times the segregation rate is controlled by the surface segregation kinetics. For long times ($\tau \gg 1$, or $t \gg \alpha_C^2 \delta^2 / D$) the asymptotic behavior of the planar solution ($\bar{d} \gg 1$) is

$$\begin{aligned} \frac{C_s - C_{s2}}{C_{s1} - C_{s2}} &= \exp(\tau)\,\mathrm{erfc}(\tau^{1/2}) \\ &= \exp\left(\frac{tD}{\alpha_C^2 \delta^2}\right)\mathrm{erfc}\left(\frac{tD}{\alpha_C^2 \delta^2}\right)^{1/2}, \end{aligned} \tag{20}$$

which clearly exhibits the limiting role of the bulk diffusion at the final stage of the segregation process. This accords with McLean's segregation kinetics model [21, 22]. A more detailed discussion of the solution is given in ref. [19].

4. EFFECTIVE THERMAL CONDUCTIVITY

Here we will use the results of $C_s(t)$ obtained in the previous section to calculate the temporal variation of the effective thermal conductivity, k_{eff}, of a porous ceramic material, following an instantaneous temperature change. In conditions close to thermal equilibrium at temperature T_1, the contribution of the steady-state heat transfer near the pore to k_{eff} of porous ceramic materials is characterized by the so-called pore-phase conductivity, k_p, which for spherical pores may be calculated as [12, 23]

$$k_p = k_{SD} + k_g = C_s \frac{\rho}{M} \frac{4\delta D_s Q^2}{dRT^2} f\left(\frac{D_s \delta}{Dd}, \frac{Q}{RT}, C_\infty\right) + k_g, \tag{21}$$

wherein, in addition to the quantities which have already been defined, k_g is the thermal conductivity of the gas filling the pore, k_{SD} denotes the contribution of the segregation–diffusion process, D_s is the diffusivity of the segregated substance along the pore surface, Q is the segregation specific enthalpy, ρ and M are the density and molar mass of the solid phase. The function f takes into account the limiting role of bulk diffusion rate on k_p [12]. The ratio k_{SD}/k_g may greatly exceed unity at low gas pressures, where the segregation–diffusion heat transfer mechanism dominates over conduction through the pores. However, at atmospheric pressure this ratio is normally less then unity (and diminishes with increasing T [12]). Thus the influence of segregation–diffusion at atmospheric pressure is less important, or even negligible.

The pore phase conductivity is the central parameter governing the temperature and gas pressure dependences of k_{eff} of porous ceramic materials. In particular, it was shown [24] that for materials characterized by heat barrier resistances associated with pore chains in the grain boundary region, the effective thermal conductivity can be calculated as

$$\frac{k_{\text{eff}}}{k_{\text{bs}}} = M\left(\frac{d}{L}, \frac{b}{d}, \frac{k_{\text{p}}}{k_{\text{bs}}}\right)(1-\varepsilon)^{3/2}, \tag{22}$$

where ε is the material porosity or void fraction, L is the average grain size, d and b are the average pore size and distance between the pores forming a pore chain (see Fig. 2), k_{bs} is the thermal conductivity of the bulk solid phase, and M is a function of the geometrical parameters and of the pore phase thermal conductivity ratio $k_{\text{p}}/k_{\text{bs}}$. The function M is graphically represented in Fig. 3. Expression (22) is valid for a wide range of porosities. For small porosities and small values of the ratio $k_{\text{p}}/k_{\text{bs}}$ expression (22) reduces to the Maxwell's formula [25].

Formula (22) is valid for equilibrium conditions. We will assume that the temporal variation of k_{eff} may also be determined by equations (21) and (22) at quasi-steady conditions, i.e. for $t > \tau_{T,H}$. In this case the constant value of C_{s} used in equation (21) for calculation of k_{p} must be substituted by the time-dependent value $C_{\text{s}}(t)$, calculated from equation (17). By so doing, one accounts for the material thermal history, as embodied in $C_{\text{s}}(t)$ and $k_{\text{p}}(t)$ when calculating the material effective thermal conductivity, $k_{\text{eff}}(t)$.

We will finally note that the above assumption implies that the steady-state analyses performed in ref. [12], which resulted in equation (21), are applicable to the quasi-steady conditions, described by $t > \tau_{\text{H}}$. In other words, small deviations from the equilibrium, associated with the slow evolution of C_{s} do not affect thermodynamic equilibrium parameters, embodied in equation (21), in particular, the specific enthalpy of segregation Q.

5. RESULTS

The results on $k_{\text{eff}}(t)$, calculated in the previous section, were compared with the data measured for the yttrium oxide ceramic (Y_2O_3), collected by a stationary method in vacuum at 600°C after a long exposure (about 100 h) at the temperature of 1400°C [5]. In this material, the oxygen vacancies in the solid crystal lattice structure play a role of impurities. Their amount segregated on pore surfaces in equilibrium is assumed to be governed by the McLean's segregation isotherm [1, 16]

$$C_{\text{s}} = \frac{C\exp(Q/RT)}{1 + C\exp(Q/RT)}. \tag{23}$$

This equation and other data [1] were used to evaluate the coefficient α_{C} in equation (14)

$$\alpha_{\text{C}} = \frac{\exp(Q/RT)}{[1 + C\exp(Q/RT)]^2} \tag{24}$$

and the dimensionless parameter $\bar{d} = d/\alpha_{\text{C}}\delta$, which for the temperature 600°C was found of order 1 for pores of diameter 0.1 μm and ~ 10 for 1 μm pores. The nondimensional complex μ was evaluated to be of order 1 by comparing with experimental data on metals [19].

Figure 4 depicts the evolution of concentration of oxygen vacancies on the surfaces of pores of 1 μm diameters in Y_2O_3, calculated from equation (17). At $t < 0$ the sample temperature was $T_1 = 1400$°C. For $Q = 57$–71 kJ mole^{-1} the corresponding equilibrium concentration is $C_{\text{s}} \approx C = 0.1\%$. Beginning from

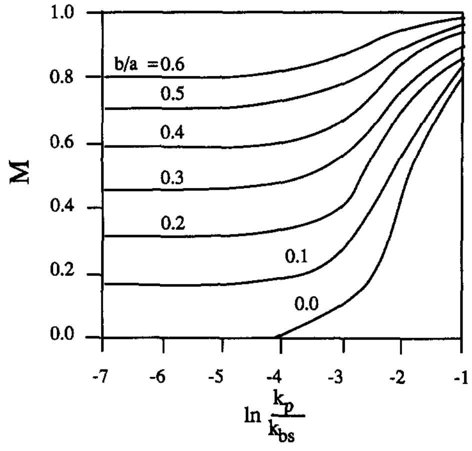

Fig. 3. Function M, used in equation (22), $d/L = 10^{-2}$.

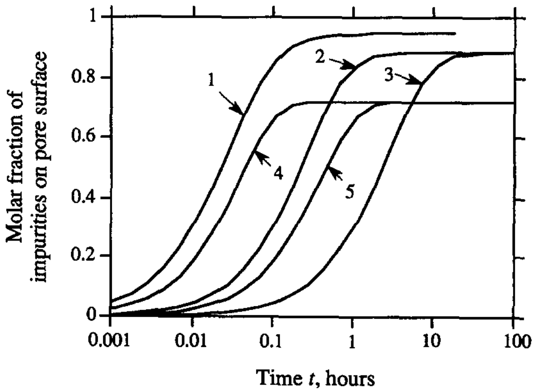

Fig. 4. Temporal dependence of the molar fraction, C_{s} of impurities on pore surfaces in Y_2O_3 after the instantaneous temperature change. (1) $Q = 71$ kJ mole^{-1}, $D = 10^{-15}$ m^2 s^{-1}; (2) $Q = 65$ kJ mole^{-1}; $D = 10^{-14}$ m^2 s^{-1}; (3) $Q = 65$ kJ mole^{-1}, $D = 10^{-15}$ m^2 s^{-1}; (4) $Q = 57$ kJ mole^{-1}; $D = 10^{-14}$ m^2 s^{-1}; (5) $Q = 57$ kJ mole^{-1}; $D = 10^{-15}$ m^2 s^{-1}.

$t = 0$ its temperature was assumed $T_2 = 600°\mathrm{C}$ (in accordance with the model discussed in Section 2). One can calculate from equation (23) the corresponding equilibrium surface concentration at 600°C: $C_s = 72$–95%. Figure 4 shows that the oxygen vacancies reach equilibrium concentration on surfaces of 1 μm pores (which corresponds to $\bar{d} \approx 1$) in about 10–30 h. However, for larger pores (with $\bar{d} \approx 10$) this process may take more than 100 h.

Unfortunately no data are available on the reaction constants K for ceramic materials. However, this quantity may be estimated as [21]

$$K\delta \leqslant D.$$

This inequality may be used to calculate K using for oxide ceramics [1, 19] $D = 10^{-14} - 10^{-16}\ \mathrm{m^2\ s^{-1}}$, $\delta = 10^{-8}$ m. This yields $K \leqslant 10^{-8} - 10^{-6}\ \mathrm{m\ s^{-1}}$.

These estimates were used as basic reference values for calculating temporal variation in the effective thermal conductivity of Y_2O_3 following the temperature change from 1400 to 600°C. The results (see Fig. 1) were obtained using the data in Fig. 4 and equations (21) and (22) for 1 μm pores, bulk diffusivity coefficient $D = 10^{-14}\ \mathrm{m^2\ s^{-1}}$ [17, 18] and reaction constants $K = 10^{-6}$, 10^{-9} and $10^{-10}\ \mathrm{m\ s^{-1}}$. The curves calculated for the first two values of K fit the experimental data for $t > 10$ h. The value $K = 10^{-10}\ \mathrm{m\ s^{-1}}$ is seen to underestimate the rate of increase of k_{eff} with time. For earlier times ($t < 10\ h$) most of the experimental values of k_{eff} lie between the curves corresponding to $K = 10^{-6}$ and $10^{-9}\ \mathrm{m\ s^{-1}}$. Therefore, these values of K may be approximately taken as upper and lower limits for the kinetic reaction constant in yttrium oxide ceramics.

The developed surface segregation kinetic model was used [19] to analyze experimental data on surface segregation rates in several two-component metal systems. The analyses yielded similar values of the kinetic constant K (of the order of $10^{-5}\ \mathrm{m\ s^{-1}}$).

One can observe an increase of k_{eff}, which is caused by an increase of the pore-phase conductivity k_p. The latter quantity is proportional to the surface concentration C_s of the oxygen vacancies, which changes with time (see Fig. 4). This temporal dependence of k_{eff} predicted by the theoretical solution satisfactorily agrees with the experimental data. In particular, both theory and measurements show that k_{eff} achieves its stationary value after about 15–20 h.

The results on temporal dependence of k_{eff} here obtained, explain poor reproducibility of thermal conductivity measurements, performed at 400°C in vacuum on Y_2O_3-based sintered ceramic samples [4, 5]. The calculations, performed for two similar samples rapidly (during one hour) cooled to 400°C: one—from 500°C and the other—from 1400°C, show that their k_{eff} may differ by as much as 40%. It clearly exemplifies the degree of the influence of the material thermal history on the effective thermal conductivity in vacuum and at low temperature.

An important consequence of the analysis is that the thermal conductivity of ceramic samples in vacuum may depend on the measurement method. For example, thermal conductivity measured by the stationary method may differ from the data collected by the monotonous heating method. Indeed, in the latter method measurements are performed at temperatures monotonously changing with the rate much exceeding the rate of changing of concentration of impurities on pore surfaces. Thermal diffusivity is, thus, calculated from the measurements, performed at surface concentrations which are not consistent with the (constantly changing) temperature. Therefore, the data obtained by this method may differ significantly (especially for low pressure) from the comparable data collected by the stationary method. However, this effect is suppressed under the atmospheric pressure conditions, where $k_p \approx k_g$.

Figure 5 displays the time variation of k_{SD} after an instantaneous change of the sample temperature. The curves are calculated on the basis of equation (21) with $C_s(t)$ calculated by inverting equation (17). The results are presented in the form

$$k_{\mathrm{SD}}(\tau) = \frac{k_{\mathrm{SD}}(\tau) - k_{\mathrm{SD}}(0)}{k_{\mathrm{SD}\infty} - k_{\mathrm{SD}}(0)} \tag{25}$$

for different values of the nondimensional parameters μ and $\bar{d}$. The results depend implicitly on T_2 via the temperature dependence of D, K and α_{C}. Here $k_{\mathrm{SD}}(0)$ corresponds to the measurement performed immediately after the change of the sample thermal conditions and $k_{\mathrm{SD}\infty} = k_{\mathrm{SD}}(\tau \to \infty)$ stands for the ultimate value of the pore phase conductivity, which can be calculated from equations (21) and (23).

When the pores in the material are sufficiently large (e.g. $\bar{d}/2 > 10$), the data calculated for a spherical pore are indistinguishable from those obtained for the flat pore surface. However, as the pore radius becomes smaller (and so does its surface area), the redistribution of impurities occurs more rapidly and, accordingly, the pore phase conductivity achieves its steady-state value in a shorter time period. One can also see that for small μ (diffusion-controlled process) the pore radius significantly influences the time variation of k_{SD}, whence for large μ its influence is much weaker.

The graphs, shown in Fig. 5, combined with equation (22), can be used for the calculation of the time variation of the effective thermal conductivity of the ceramic material on the basis of knowledge of the material physical properties and microstructure.

6. CONCLUSIONS

(1) The influence of the segregation kinetics on the temporal behavior of the effective thermal conductivity of the porous ceramics is elucidated. The analysis shows that the kinetics of the impurities' segregation process, induced by changing material temperature, significantly influences the effective thermal

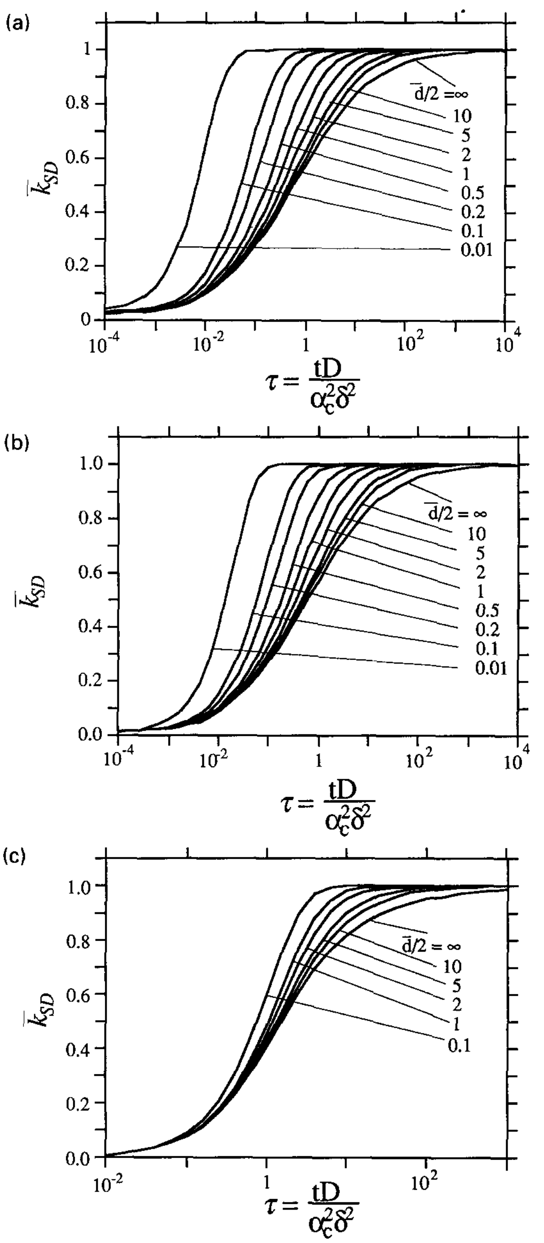

Fig. 5. Temporal dependence of the nondimensional pore phase conductivity for various values of parameter μ and $\bar{d}$. (a) $\mu = 0$; (b) $\mu = 0.01$; (c) $\mu = 1$.

conductivity of porous ceramics, especially in vacuum conditions and in the temperature range 400–1000°C. The segregation–diffusion process is shown to be a factor responsible for scatter of experimental data collected in vacuum and at low temperatures. Dependence of k_{eff} of similar samples on the measurement method and the material thermal history are shown to be also attributable to this heat transfer mechanism.

(2) A physico-mathematical model describing kinetics of the surface segregation process is suggested. The model allows the obtaining of analytical solutions exhibiting simple short- and long-time asymptotic behaviors of the surface segregated concentrations.

(3) The influence of the pore radius on the temporal behavior of k_{eff} is quantified by the parameter $\bar{d} = d/\alpha_C\delta$. For $\bar{d} > 10$ the effect of the curvature of the pore surface on the segregation process can be neglected.

(4) The experimental data collected for $k_{\text{eff}}(t)$ of Y_2O_3 after an instantaneous change of the sample temperature from 1400 to 600°C were compared with the predictions of the model. It is shown that the model satisfactorily correlates $k_{\text{eff}}(t)$. More experimental data are needed to fully assess the predictive capacity of the model.

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