

Influence of segregation–diffusion processes on the effective thermal conductivity of porous ceramics

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Abstract—A model of heat transfer in porous ceramics in the presence of segregation–surface diffusion mechanism is proposed. The effective thermal conductivities of materials possessing a small amount of spherical or cylindrical pores are calculated, which are shown to generalize the Maxwell formula for conductivities of composite materials. Nondimensional parameters are formulated which govern the relative influence of segregation and diffusion of impurities on the effective conductivity of porous materials. Estimates performed for Arrhenius and McLean surface isotherm formulas show that the segregation–diffusion mechanism satisfactorily describes abnormal temperature dependences of thermal conductivities of refractory oxides in vacuum.

1. INTRODUCTION

HEAT TRANSFER processes in high temperature ceramics and refractory materials are governed by their thermophysical properties, primarily, thermal conductivity and thermal diffusivity. Dependences of these properties upon the gas pressure and temperature determine thermal regimes of various high-temperature aggregates, insulating layers, etc. Investigation of gas pressure and temperature dependences of these properties in ceramic materials is an important problem, lying in the focus of numerous theoretical and experimental studies [1–10].

Primary scientific and engineering interest is concentrated on measuring and predicting the effective thermal conductivity, k_{eff} of various ceramic materials in the temperature range of 300–2000 K, and gas pressure ranging from 1 to 10^{-5} atm. Behaviour of k_{eff} of ceramics in the above conditions depends upon the material's chemical composition and its porous microstructure.

Thermal conductivities of dense, sintered polycrystalline metal oxides (Al_2O_3 , MgO , Y_2O_3 , BeO , etc.), possessing almost zero porosity, ε decrease with increasing temperature in the range 200–1000°C. This behaviour, which is normally observed both at atmospheric air pressure and in vacuum, accords with the Eucken law [11], which was found experimentally and afterwards confirmed theoretically on the basis of classical solid state physics models [12].

For most ceramics and insulating materials, where porosities may range from 10 to 90% and above, k_{eff} was evaluated using Maxwell type models [5, 13–16] for the effective thermal conductivity of a composite material, possessing two phases: one, solid (crystalline), with thermal conductivity k and another, porous (gaseous), with thermal conductivity k_g . In particular, for low porosity the Maxwell formula yields

$$k_{\text{eff}}/k = (1 - 2\Psi_M)/(1 + \Psi_M), \quad (1)$$

where

$$\Psi_M = \varepsilon \frac{k - k_g}{2k + k_g}. \quad (2)$$

Since the thermal conductivity of the solid phase, $k(T)$, decreases with temperature according to the Eucken law, the effective thermal conductivity for this composite material calculated from equations (1) and (2) also follows this temperature dependence. This trend is indeed observed for atmospheric pressure [2–6].

However, effective thermal conductivities of many porous materials significantly decrease with decreasing gas pressure. This phenomenon, which was most clearly observed for temperatures of about 400°C, is explained by the influence of thin gaps and pore chains, separating sintered granules of ceramic materials [10]. In addition, thermal conductivities of several porous ceramics, measured in vacuum, were found to violate the Eucken law [2–6]. In particular, for low air pressure k_{eff} of Al_2O_3 , MgO , Y_2O_3 were found to *increase* with temperature increasing from 200–1000°C, which contradicts the Eucken law, predicting a decrease of thermal conductivity in this range. It is worth mentioning that for the above materials, k_{eff} at $T \approx 1000^\circ\text{C}$ reaches the value, obtainable from the Maxwell type models with k_g approximately equal to thermal conductivity of air at atmospheric pressure (about $0.05 \text{ W m}^{-1} \text{ K}^{-1}$).

The above abnormal temperature and pressure dependences of k_{eff} pointed at the existence of additional heat transfer mechanisms governing the behaviour of k_{eff} at low pressures and temperatures about 1000°C. It was attempted to explain this abnormal behaviour of k_{eff} by assuming that at high temperatures the pores no longer contain vacuum but,

This paper is aimed at developing a quantitative physico–mathematical model of heat transfer processes within porous ceramic materials, occurring in the presence of segregation–surface diffusion of impurities. The specific goal of this study is the investigation of the effect of this process on the effective thermal conductivity of porous materials. Our rigorous analyses are based on the classical Maxwell calculations of electric (thermal) conductivities of composite materials, which models are generalized to include the segregation–surface diffusion mechanism. On the basis of the fundamental treatment proposed here, the *ad hoc* model developed in ref. [7] is reviewed and its basic assumptions are scrutinized and revised.

2. SEGREGATION–SURFACE DIFFUSION MECHANISM OF HEAT TRANSFER IN POROUS MATERIALS

The solid phase of porous ceramics usually contains various kinds of impurities, which can be substances of different chemical composition. Alternatively, in pure crystalline materials, such impurities may be defects of the lattice structure [13, 17]. Every pore is surrounded by a thin surface layer possessing a distorted lattice structure [13] (see Fig. 1). In this layer the energy, e , of occupation of distorted surface locations by an impurity atom is less than the comparable occupation energy, E for undistorted lattice sites, far from the surface. The difference, $E - e$ between the occupation energies leads to the segregation of the impurities in the surface layer, where the volumetric concentration C_s is much larger than the

comparable concentration C , prevailing in the bulk [17, 18].

Migration of the impurity atoms in the surface layer is characterized by lower activation energy, compared with that prevailing within the undistorted crystal lattice. Therefore, motion of impurities in the surface layer occurs by almost free passing from one distorted site to another. This is fundamentally different from the comparable motion in the bulk phase, where the impurities' atoms move by squeezing between the surrounding atoms of the crystal lattice. Therefore, the impurities' surface atomic mobility is greater than its mobility in the bulk and, hence, the surface diffusivity, D_s is greater than the bulk diffusivity, D . Experimental data show that in sintered polycrystalline ceramics D_s exceeds D by the factor of order 10^6 and more [13, 19].

In the absence of temperature gradients any ceramic material possessing temperature T_0 is characterized by the corresponding equilibrium values C_{s0} , C_0 of the surface and the bulk species concentrations, related by the surface isotherm

$$C_{s0} = f(C_0, T_0). \quad (3)$$

In the equilibrium state there are no mass or heat fluxes within the material.

Consider now a *steady-state* heat and mass transfer process, resulting from an external macroscopic temperature gradient, imposed on the material. Since the temperature along the pore surface is not uniform, the equilibrium homogeneous distribution (3) of the surface species concentration and the bulk concentration is now distorted. We will assume that the equilibrium, described by equation (3), prevails *locally*, in each point of the pore surface, namely,

$$C_s = f(C, T). \quad (4)$$

Since C_s normally decreases with increasing T , the 'cooler' site of the pore surface will possess higher surface concentration than that prevailing on the 'hotter' site. The resulting nonuniform surface concentration distribution causes diffusive flux from the cooler site to the hotter site of the pore surface. This is accompanied by the concomitant segregation process; namely the impurities are segregated from the pore boundary region onto the cooler pores' sites, and dissolved (desegregated) from the hotter pores' sites. The above segregation–desegregation processes are accompanied by diffusion of impurities in the bulk and the pore boundary region, as well as by heat release on the cooler sites and absorption on the hotter sites. The temperature field around the pore is thus distorted due to the heat release and absorption, resulting thereby in an additional heat flux across the pore, compared with conductive flux prevailing in the absence of segregation–diffusion mechanism. This extra heat flux is responsible for the concomitant increase of the effective thermal conductivity, k_{eff} , of the porous ceramic material.

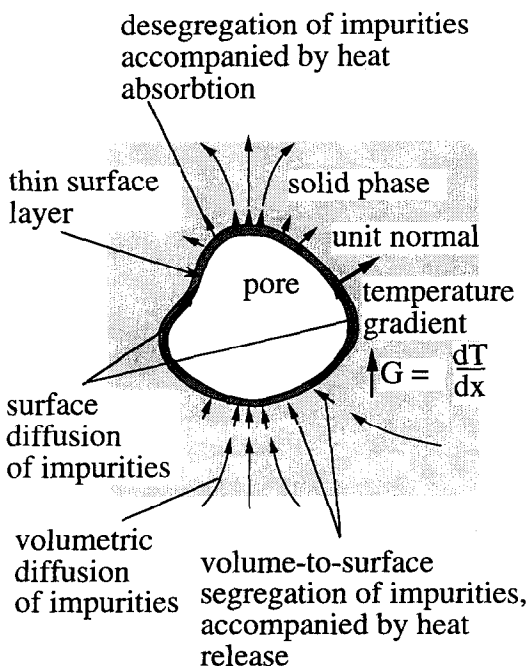


FIG. 1. Heat conduction, segregation, bulk and surface diffusion processes within porous ceramic materials.

The temperature fields inside and outside the pore are described by the Laplace equation:

$$\nabla^2 T = 0. \quad (5)$$

The volumetric concentrations in the bulk and the grain boundary regions are also governed by the Laplace equation:

$$\nabla^2 C = 0. \quad (6)$$

Assuming that the mass transfer in the thin layer δ occurs along the pore surface, and the impurities do not penetrate into the gas within the pore, one can write the equation of the impurities mass conservation at the surface in the form

$$\delta D_s \nabla_s^2 C_s = -D\mathbf{n} \cdot \nabla C \quad \text{on the pore surface,} \quad (7)$$

where ∇_s is the surface gradient operator and \mathbf{n} is the vector unit normal to the surface and directed inside the bulk phase.

The following boundary condition relates the heat and mass fluxes on the pore surface:

$$k\mathbf{n} \cdot (\nabla T)_{\text{solid}} - k_g \mathbf{n} \cdot (\nabla T)_{\text{gas}} = -Q D\mathbf{n} \cdot \nabla C \quad \text{on the pore surface,} \quad (8)$$

where Q is the specific heat release of the segregation process. This equation describes balance between the conductive heat fluxes in the gas and the solid phase, and the heat released (absorbed) due to the segregation (desegregation) processes.

Equations (4)–(8) constitute a general model of the heat and mass transfer processes occurring in two-phase (or even multiphase) materials in the presence of segregation–diffusion processes. This model combined with the knowledge of the geometric pore microstructure and material's chemical composition may be used to study the influence of the latter processes on the (coarse-scale) thermal conductivity of a composite ceramic material and the effective diffusivity of impurities in it.

Calculation of heat transfer in porous ceramic materials, possessing complicated grain boundary structure, lies beyond the scope of the present study. Here we will investigate the role of the segregation–surface diffusion processes on the basis of the simple Maxwell-type model for thermal conductivity of a solid material, possessing a small amount of spherical pores. As will be shown in the following sections, in this case the above equations (4)–(8) may be rigorously solved.

We will be specifically interested in the heat and mass transfer processes occurring in the region separating two partially sintered granules (grain boundary region). The solid structure in this region differs significantly from that prevailing at large distances from the pore boundary [13, 19]. The grain boundary is characterized by a less dense packing of atoms within the lattice, which results in greater atomic mobility and a lower activation energy for diffusion, than the comparable quantities prevailing within the undis-

torted lattice structure [13]. It is estimated that the diffusivity of impurities D^* in the grain boundary region possesses a somewhat intermediate value between the bulk and the surface diffusivities, i.e. $D < D^* < D_s$.

3. PHYSICO–MATHEMATICAL MODEL

Ceramic material will be viewed as a solid with thermal conductivity k , containing uniformly distributed spherical pores characterized by a low volumetric concentration ε (see Fig. 2). The pores are filled with a neutral gas possessing thermal conductivity k_g . In order to estimate the contribution of segregation–surface diffusion processes to the heat transfer, mathematical analysis will be performed for a single pore (Fig. 1) within an effectively infinite solid material, embodied in a temperature field, characterized by uniform gradient $G = dT/dx$ at infinity.

The different mass transfer properties prevailing near a pore within a ceramic material are appropriately reflected in the three-layer heat and mass transfer model: surface layer, of small thickness, $\delta \ll a$, pore boundary layer, $a < r < b$, possessing the properties of grain boundary region, and the bulk region, $r > b$ (see Fig. 2).

Equations (5)–(8) may be rewritten in the spherical coordinate system (Fig. 3). In the spherical coordinate system equation (7) adopts the form:

$$D_s \delta \frac{1}{a^2} \frac{d}{d\theta} \left(\sin \theta \frac{dC_s}{d\theta} \right) = -D^* \frac{\partial C}{\partial r} \Big|_{r=a}. \quad (9)$$

Far from the pore surface both the temperature and the concentration fields are undisturbed, i.e.

$$T \rightarrow T_0 + Gr \cos \theta, \quad C \rightarrow C_0, \quad r \rightarrow \infty. \quad (10)$$

The boundary condition (8) in the chosen system is:

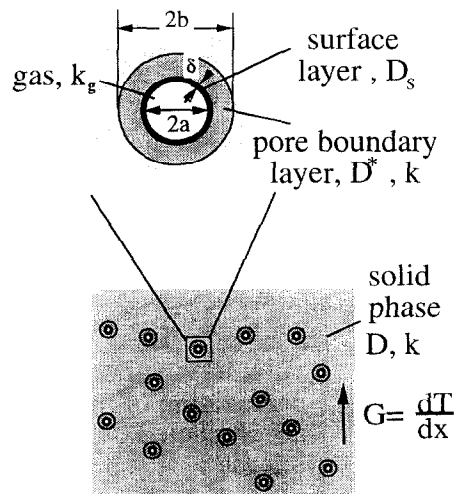


FIG. 2. Physico–mathematical model.

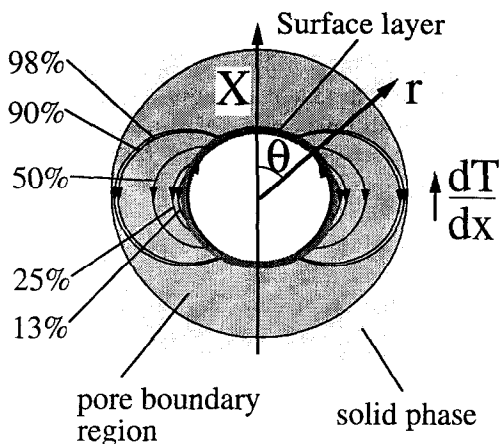


FIG. 3. Transport of impurities in the vicinity of a pore, induced by an externally applied temperature gradient.

$$k \frac{\partial T}{\partial r} \Big|_{r=a+0} = -QD^* \frac{\partial C}{\partial r} \Big|_{r=a} + k_g \frac{\partial T}{\partial r} \Big|_{r=a-0}. \quad (11)$$

Additional boundary conditions require continuity of temperature at the pore surface and continuity of the volumetric concentration and the mass fluxes across the pore boundary surface:

$$T|_{r=a-0} = T|_{r=a+0}, \quad (12a)$$

$$C|_{r=b-0} = C|_{r=b+0}, \quad D^* \frac{\partial C}{\partial r} \Big|_{r=b-0} = D \frac{\partial C}{\partial r} \Big|_{r=b+0}. \quad (12b, c)$$

The problem posed by equations (5), (6), (9)–(12) should be solved jointly with the equilibrium isotherm equation (4). In order to simplify the solution we will linearize the functional dependence (4) in the following form:

$$C_s = C_{s0} + \alpha_T(T - T_0) + \alpha_C(C - C_0), \quad (13)$$

where the coefficients

$$\alpha_T = \left(\frac{\partial C_s}{\partial T} \right) \Big|_{C_0, T_0}, \quad \alpha_C = \left(\frac{\partial C_s}{\partial C} \right) \Big|_{C_0, T_0} \quad (14)$$

are evaluated at the equilibrium values C_0 , T_0 .

4. SOLUTION

The solution of equations (5), (6) is

$$T = Ga \sum_{n=0}^{\infty} c_n \frac{r^n}{a^n} P_n(\cos \theta), \quad r \leq a, \quad (15a)$$

$$T = T_0 + Gr \cos \theta + Ga \sum_{n=0}^{\infty} a_n \frac{a^{n+1}}{r^{n+1}} P_n(\cos \theta), \quad r > a, \quad (15b)$$

$$C = Ga \frac{\alpha_T}{\alpha_C} \sum_{n=0}^{\infty} \left(d_n \frac{r^n}{a^n} + f_n \frac{a^{n+1}}{r^{n+1}} \right) P_n(\cos \theta), \quad a < r \leq b, \quad (16a)$$

$$C = C_0 + Ga \frac{\alpha_T}{\alpha_C} \sum_{n=0}^{\infty} b_n \frac{a^{n+1}}{r^{n+1}} P_n(\cos \theta), \quad r > b, \quad (16b)$$

where $P_n(\cos \theta)$ are the Legendre polynomials, a_n , b_n , c_n , d_n and f_n are unknown constants.

Equations (9)–(12) can be satisfied for arbitrary θ if $a_n = b_n = c_n = d_n = f_n = 0$ for $n > 1$, $a_0 = b_0 = f_0 = 0$,

$$c_0 = \frac{T_0}{Ga}, \quad d_0 = \frac{C_0}{Ga} \frac{\alpha_C}{\alpha_T},$$

and

$$a_1 = \Gamma_v \{ (K_C + 1)(1 - k_g/k) - 2K_T + v[(2K_C - 1)(1 - k_g/k) + 2K_T] \},$$

$$b_1 = -9\Gamma_v K_C D^* / (D^* + 2D),$$

$$c_1 = 3\Gamma_v [K_C + 1 + v(2K_C - 1)],$$

$$d_1 = -6\Gamma_v v K_C, \quad f_1 = -3\Gamma_v K_C,$$

where

$$v = (a/b)^3 (D^* - D) / (D^* + 2D), \quad (17)$$

$$\Gamma_v = \{ (K_C + 1)(2 + k_g/k) + 2K_T + v[(2K_C - 1)(2 + k_g/k) - 2K_T] \}^{-1}, \quad (18)$$

with the nondimensional parameters

$$K_C = \frac{D_s}{D^*} \frac{\delta}{a} \alpha_C, \quad K_T = -\frac{D_s Q \alpha_T}{k} \frac{\delta}{a}. \quad (19a, b)$$

Parameters K_T , K_C characterize the relative influence of segregation–diffusion processes on the heat transfer in porous materials and will be discussed in the following section.

The final solution of the problem is obtained by substitution of the above coefficients into (15a, b), (16a, b):

$$T(r, \theta) = T_0 + 3G\Gamma_v [K_C + 1 + v(2K_C - 1)] r \cos \theta, \quad 0 < r \leq a, \quad (20)$$

$$T(r, \theta) = T_0 + Gr \cos \theta + G\Gamma_v \left\{ (K_C + 1) \left(1 - \frac{k_g}{k} \right) - 2K_T + v \left[(2K_C - 1) \left(1 - \frac{k_g}{k} \right) + 2K_T \right] \right\} \cos \theta \frac{a^3}{r^2}, \quad r > a, \quad (21)$$

$$C_s(\theta) = C_{s0} + 3G\alpha_T \Gamma_v (1 - v) a \cos \theta, \quad (22)$$

$$C(r, \theta) = C_0 - 3G \frac{\alpha_T}{\alpha_C} \Gamma_v K_C \left(2vr + \frac{a^3}{r^2} \right) \cos \theta, \quad a < r \leq b, \quad (23)$$

$$C(r, \theta) = C_0 - 9G \frac{\alpha_T}{\alpha_C} \Gamma_v K_C \frac{D^*}{D^* + 2D} \cos \theta \frac{a^3}{r^2}, \quad r > b. \quad (24)$$

The impurities flux calculated for typical (for small pores) values of parameters $b/a = 2$ and $D_s/D^* = 100$ [13,16] from solutions (23), (24) are exhibited in Fig. 3. One can see that the mass vector flux lines are closed, i.e. start from and terminate on the pore surface. In that sense the segregation–diffusion mechanism is analogous to mass transfer processes occurring in heat pipes [20]. It is important to note that for the above choice of parameters $a, b, D_s/D^*$ the major portion of the mass stream (98%) is transferred in the pore boundary layer. This means that for the values of parameters specified above, the temperature and volumetric concentration fields reach their asymptotic values (prevailing far from the pore) within the pore boundary region and the comparable processes in the bulk may be disregarded. The solution for the concentration distribution in this case may be obtained from (23) upon setting $v = 0$ and extending $b \rightarrow \infty$. Indeed, it can be easily shown that for small pores ($2a < 1 \mu\text{m}$) and the values of parameters specified above, $v \ll 1$. Therefore, we can set $v = 0$ in (20)–(24).

For $v = 0$ the temperature distribution in the material and the concentrations of impurities in the pore surface and bulk regions, adopt the forms

$$T(r, \theta) = T_0 + Gr \cos \theta + G\Gamma_0$$

$$\times \left[(K_C + 1) \left(1 - \frac{k_g}{k} \right) - 2K_T \right] \cos \theta \frac{a^3}{r^2}, \quad r > a, \quad (25)$$

$$C_s(\theta) = C_{s0} + 3G\alpha_T \Gamma_0 a \cos \theta, \quad (26)$$

$$C(r, \theta) = C_0 - 3G \frac{\alpha_T}{\alpha_C} \Gamma_0 K_C \cos \theta \frac{a^3}{r^2}, \quad r > a. \quad (27)$$

where

$$\Gamma_0 = \left[(K_C + 1) \left(2 + \frac{k_g}{k} \right) + 2K_T \right]^{-1}. \quad (28)$$

5. EFFECTIVE THERMAL CONDUCTIVITY

The effective thermal conductivity tensor of a composite material is defined as

$$\mathbf{q} = -\mathbf{k}_{\text{eff}} \cdot \nabla T, \quad (29)$$

where \mathbf{q} is a heat flux, ∇T is a temperature gradient.

Upon setting $K_T = 0$ (in the absence of segregation process), expressions (20) and (25) reduce to Maxwell's [14] solution for the temperature distribution within the material of thermal conductivity k , possessing spherical inclusions with radius a and thermal conductivity k_g :

$$T(r, \theta) = T_0 + Gr \cos \theta + G \frac{k - k_g}{2k + k_g} \cos \theta \frac{a^3}{r^2}, \quad r > a. \quad (30)$$

Solution (30) can be brought to the form (25) by means of replacing k_g by k_p given by

$$k_p = \frac{2kK_T}{K_C + 1} + k_g. \quad (31)$$

The above introduced quantity k_p will be interpreted as the thermal conductivity of the pore phase. This quantity serves as an important element in various models for the effective thermal conductivity of porous and composite materials [10, 15, 16].

Following Maxwell's treatment we can use (30), (31) to calculate the effective scalar thermal conductivity of porous material, k_{eff} : in the presence of segregation–surface diffusion processes (cf. (1)):

$$k_{\text{eff}}/k = (1 - 2\Psi)/(1 + \Psi). \quad (32)$$

In the above

$$\Psi = \varepsilon \frac{1 - k_p/k}{2 + k_p/k} \quad (33)$$

is a parameter characterizing the influence of the pore phase conductivity on the effective thermal conductivity of porous material.

In the absence of segregation process ($K_T = 0$) expressions (32), (33) clearly reduce to the Maxwell formulas (1), (2).

To understand the influence of the segregation–diffusion processes on the heat transfer, consider non-dimensional parameters K_C, K_T , defined in (19a,b). Using definitions (14) of the coefficients α_C, α_T , supposing that a characteristic temperature drop ΔT (say, equal to Ga) across the pore results in the concomitant drops ΔC and ΔC_s of the impurities' concentrations in the bulk and the surface layer regions, one can write:

$$K_T = \frac{D_s \Delta C_s \delta}{a^2} Q \frac{a}{k \Delta T} = \frac{j_s Q}{q},$$

$$K_C = \frac{D_s \Delta C_s \delta}{a^2} \frac{a}{D^* \Delta C} = \frac{j_s}{j^*},$$

where $q (=kGa)$ is the heat flux, and j_s, j^* are the respective impurities concentration fluxes in the surface and the pore boundary regions, resulting from the temperature gradient G . As such, parameter K_C determines the mass transfer rate in the surface layer with respect to the comparable mass transfer in the pore boundary region. Therefore, this parameter characterizes the limiting role of the bulk diffusion in the process of impurities' transfer into the surface layer. On the other hand, K_T governs the effect of heat transfer rate induced by the segregation–diffusion mechanism with respect to the conductive heat transfer in the pore boundary region.

The competitive influences of the above parameters may be elucidated by considering the effects of parameters K_C, K_T on the dimensionless thermal conductivity k_{eff}/k of a porous material, given by (32), (33). The above ratio depends upon the porosity ε and the physico-chemical and thermal material's properties via parameter Ψ . In particular, in the cases where $k_p < k$ ($\Psi > 0$), or $k_p > k$ ($\Psi < 0$), one respec-

tively obtains that $k_{\text{eff}} < k$ ($k_{\text{eff}} > k$). In the absence of segregation–diffusion mechanism ($K_T = 0$, $k_p = k_g$) effective thermal conductivities of all ceramic materials are usually less than the conductivity k of their solid phase, since normally $k_g < k$. However, for an intensive segregation process (large K_T), the pore phase conductivity, k_p may exceed k even in the case of evacuated pores ($k_g = 0$). In particular, when $K_T \gg (K_C + 1)/2$, corresponding to the situation, where the segregation–diffusion mechanism dominates over the conductive heat transfer, equations (32), (33) yield the effective thermal conductivity of a material possessing inclusions with infinite conductivity: $k_{\text{eff}} = k(1 + 2\varepsilon)/(1 - \varepsilon)$.

The increasing intensity of the segregation–diffusion processes (increasing K_T) leads to increase of the effective thermal conductivity. However, this effect is controlled by the grain boundary diffusion rate, characterized by K_C . Namely, decrease of pore boundary diffusion rate (increase of K_C) leads to the diminution of the influence of the segregation mechanism on k_{eff} .

The relative influence of the segregation–diffusion heat transfer mechanism with respect to heat conduction in the gas is thus governed by the non-dimensional parameter, elucidated from (31):

$$\omega = \frac{k}{k_g} \frac{2K_T}{K_C + 1}. \quad (34)$$

Namely, the inequalities $\omega \gg 1$, $\omega \ll 1$ respectively describe the situations, where the segregation–diffusion mechanism dominates over the gas conduction (as in the case of low gas pressures) or is insignificant (e.g. for atmospheric gas pressure). Qualitative estimates of the relative influence of the above two heat transfer mechanisms for various temperatures are performed in the following section.

In the two-dimensional case where the pore may be approximated by an infinite circular cylinder, similar calculations yield $k_{\text{eff}} = (1 - \Psi)/(1 + \Psi)$, where

$$\Psi = \varepsilon \frac{1 - k_p/k}{1 + k_p/k}, \quad (35)$$

and the pore phase conductivity for cylindrical geometry is

$$k_p = \frac{kK_T}{K_C + 1} + k_g. \quad (36)$$

It must be pointed out, that there exist more elaborate models for calculation of the effective properties of composite materials [5, 15–17, 21, 22] which are applicable to all values of material porosities. Our small ε analysis may be generalized to materials possessing a very general spatially periodic structure by application of the theory of macrotransport processes [23].

6. DISCUSSION

In this section we will estimate the influence of various parameters on the value of thermal con-

ductivity k_p of the pore phase given by equation (31). Towards this goal consider several models describing equilibrium concentration of the segregated substance.

The general Arrhenius' formula for surface concentration of impurities [13] yields

$$C_s = C^0 \exp(Q/RT), \quad (37)$$

where R is the universal gas constant and $C^0 = \text{const}$. Using this equation, together with equations (14), (19a,b) and (31), the following expression for the pore thermal conductivity is obtained:

$$k_p = \frac{mD_s Q^2 C_{s0} \delta}{RT_0^2 a} + k_g, \quad (38)$$

with $m = 2, 1$ for spherical and cylindrical pore respectively.

This result may be obtained by the following simple considerations [7]. Assume that the pore may be viewed as a circular cylinder possessing height h and base diameter d , with axis parallel to the direction of external temperature gradient and temperatures T_0 , $T_0 + \Delta T$, prevailing at the lower and the upper bases, respectively. The impurities' mass transfer rate along the lateral surface of the cylinder is

$$J = D_s \frac{C_s(T_0) - C_s(T_0 + \Delta T)}{h} \delta \pi d.$$

Expanding $C_s(T) - C_s(T + \Delta T)$ in Taylor series and using (37), one obtains

$$J = \frac{D_s Q C_s}{RT_0^2} \frac{\delta \pi d}{h} = \frac{D_s Q C^0}{RT_0^2} \frac{\delta \pi d}{h} \exp\left(\frac{Q}{RT_0}\right). \quad (39)$$

The heat-transfer rate across the pore may be expressed in the form:

$$Q'' = JQ + k_g \frac{\pi d^2}{4} \Delta T = \frac{D_s Q^2 C_s}{RT_0^2} \frac{\delta \pi d}{h} \Delta T + k_g \frac{\pi d^2}{4} \Delta T.$$

The pore conductivity, defined in terms of the above total heat transfer rate and the temperature gradient $\Delta T/h$ across the lateral cylinder surface, is:

$$k_p = \frac{Q''}{\Delta T} \frac{4h}{\pi d^2} + k_g = \frac{D_s Q^2 C_s}{RT^2} \frac{4\delta}{d} + k_g,$$

which coincides with (38).

As one can see from equation (39), the amount of impurities transferred across the pore per unit time does not depend on their volumetric concentration in the vicinity of the pore surface. Therefore equation (38) implies that there is an endless source of segregated substance on the pore surface, maintaining a steady stream of impurities (39).

Moreover, since the Arrhenius' formula does not take into account the relationship between the bulk and surface concentration of the segregated substance, expression (38), derived on its basis, completely disregards the limiting role of the volumetric diffusion rate in the segregation–diffusion heat transfer mechanism.

Kingery [13, 17], following McLean [18], suggested another expression relating equilibrium bulk and surface concentrations of impurities in ceramics:

$$C_s = \frac{AC \exp\left(\frac{Q}{RT}\right)}{1 + A \frac{C}{\rho} \exp\left(\frac{Q}{RT}\right)} \quad (40)$$

where A is a nondimensional constant, which is approximately equal to unity [17], ρ is the density of the solid phase. This expression allows us to account for the influence of the bulk diffusion on the pore phase conductivity. Expression (40), jointly with equations (14), (19a,b) and (31), lead to the following formula for k_p :

$$k_p = \frac{mD_s Q^2 C_0 \delta}{RT_0^2 a} \left\{ \frac{D_s \delta}{D^* a} + \frac{1}{A} \left[1 + A \frac{C_0}{\rho} \exp\left(\frac{Q}{RT_0}\right) \right]^2 \exp\left(-\frac{Q}{RT_0}\right) \right\}^{-1} + k_g = k_{ps} + k_g \quad (41)$$

Comparing k_p calculated for typical values of parameters, one can show that formulas (39) and (41) yield close values of the pore phase conductivity for temperatures of about 1000°C, in which case almost all segregated substance is dissolved in the bulk phase. However, for moderate temperatures (about 400°C), the Arrhenius formula yields significantly higher values of k_p than the expression (41) obtained using Kingery–McLean relationship (40). This disparity is clearly explained by the ‘endless impurity source’ approximation, implicitly used in the Arrhenius formula.

Expression (41) will be further used to delineate the temperature range for which the influence of the segregation–diffusion mechanism is comparable to that of the heat conductive transport through the gas, expressed by the value k_g in equation (41). Towards this aim compare the latter quantity with the first term, k_{ps} appearing in the right hand side of (41).

The results of calculations of k_{ps} in accordance with expression (41) are exhibited on Fig. 4. The following

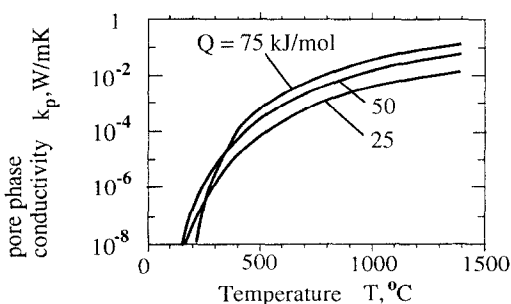


FIG. 4. Dependence of the pore phase conductivity of Y_2O_3 in vacuum on temperature for several values of the specific heat release, associated with segregation of oxygen vacancies in crystal lattice.

data were used: the energy of segregation $Q = 25$ – 75 kJ mol^{-1} [17]; the temperature dependence for the surface diffusion coefficient: $D_s = D_{s0} \exp(-E/RT_0)$, with $D_{s0} = 0.0606 \text{ m}^2 \text{ s}^{-1}$, $E = 81.9 \text{ kJ mol}^{-1}$, as for diffusion of oxygen vacancies in Y_2O_3 [7]; $(\delta D_s)/(aD^*) = O(1)$, in accordance with results of grain boundaries investigations and typical relationships between surface and grain boundary diffusion coefficients in refractory oxides [13, 17].

One can see that the effect of segregation–diffusion mechanism upon the thermal conductivity of Y_2O_3 is manifested in growth of the pore thermal conductivity k_{ps} from about 10^{-6} to $5 \times 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$ in the range of temperatures from 400 to 1200°C. The lower limit accords with the values of thermal conductivity of rarefied gases. The upper limit is comparable with the thermal conductivity, k_g of the air at the atmospheric pressure [16]. As such, one can conclude that for atmospheric pressure and moderate temperatures $k_{ps} \ll k_g$, whereas for higher temperatures (about 1200°C) these quantities are of the same order of magnitudes.

The results shown in Fig. 4 explain the growth of the effective thermal conductivity of Y_2O_3 in vacuum in the range 400–1200°C, experimentally measured [6] on high purity samples sintered in vacuum at 2000°C. This procedure insures the absence (within the above-mentioned temperature range) of competitive heat transfer mechanisms [5, 9, 10], such as gas emission or alteration of the porous structure of the material during the heating. The measured temperature behaviour of k_{eff} was shown to be attributable to increase of k_p from $10^{-6} \text{ W m}^{-1} \text{ K}^{-1}$ at 400°C to $5 \times 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$ at 1200°C, which is clearly confirmed by Fig. 4.

The heat and mass transfer in porous ceramic materials in the presence of segregation–diffusion processes possess an important feature, which is the closed form of the mass flux line, induced by the macroscopically homogeneous temperature gradient. This means that a piece of ceramic material transmits zero net mass across its external faces. This heat-pipe like property clearly rectifies the unnecessary assumption about the endless ‘external’ source of impurities, made in refs. [7, 8]. This property may be shown to be reciprocal with respect to the transport of heat and impurities: that is, a macroscopic gradient of volumetric concentration, C , applied to an *isothermal* porous material will induce heat transfer processes in which the heat flux lines start and terminate on the pore surfaces. However, the net heat flux transferred through the material will be zero.

7. CONCLUSIONS

1. Heat and mass transfer processes occurring within porous ceramic materials in the presence of segregation–diffusion processes are described by the generic physico–mathematical model. It is shown that an external temperature gradient applied to a ceramic

material induces circulation of impurities along closed lines in the vicinity of pores.

2. The Maxwell formula for the effective thermal conductivity of continuous materials with disperse spherical (or cylindrical) pores is generalized to include the effect of segregation–volumetric surface diffusion mechanism for an arbitrary segregation isotherm, linearized in the vicinity of the equilibrium state. The limiting role of volumetric diffusion on the effective thermal conductivity is quantified in terms of the pertinent nondimensional parameters.

3. The general expression for the effective thermal conductivity is used to calculate the pore phase conductivity, k_p , which quantity is used for interpretation of the experimental data. In a particular case of the Arrhenius segregation isotherm the expression for k_p reduces to the formula previously obtained in simplistic analysis [7, 8]. The expression for k_p , obtained on the basis of the Kingery–McLean segregation isotherm, establishes the relative influence of the segregation–diffusion heat transfer mechanism with respect to the conductive heat transfer through the gas in pores.

4. The physico–mathematical model developed in the present paper allows us to explain the violation of the Eucken law in vacuum, exhibited by refractory metal oxides; namely, the growth of the function $k_{\text{eff}}(T)$ in the temperature range 500–1000°C and above.

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