

A METHOD FOR DETERMINING THE BARODIFFUSION COEFFICIENT OF LIQUID IN CERAMIC SUSPENSION, DESCRIBING ITS BEHAVIOUR ON POURING INTO A POROUS FORM

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The effect of the pressure gradient on the transfer of liquid through the ceramic mix during the pouring of the slip into a ceramic mould was studied. A method, based on suction of the liquid through a layer of porous material, where the suspension at the frit is subject to the effect of a pressure difference, was devised for determining the barodiffusion pressure. The barodiffusion coefficient was found to be independent of pressure, and its value for barodiffusion of water in a suspension of $\alpha\text{-Al}_2\text{O}_3$ was established as being $3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$.

INTRODUCTION

A study of the transfer of liquid during the body formation and solidification in the case of slip casting (pouring of the ceramic suspension into a porous mould), based on the generalized diffusion theory, has given evidence for the significance of the effect of the state of the boundary on the transfer of the liquid phase. In the instance of a saturated boundary, the liquid transfer was induced solely by the concentration gradient, with the corresponding diffusion coefficient $D = 2.45 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ [1]. In the case of an unsaturated boundary, the effective diffusion coefficient $D_{\text{ef}} = 2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ was determined. The difference of an order of magnitude between the two diffusion coefficients was attributed to the effect of capillary barodiffusion, which speeds up the liquid transfer by the effect of capillary suction in the menisci at the unsaturated boundary [2].

The present study was concerned with establishing the effect of the pressure gradient on the liquid transfer in the unsaturated boundary, and with devising a method for experimental determination of the barodiffusion coefficient.

THEORETICAL PRINCIPLES OF THE METHOD FOR MEASURING CAPILLARY BARODIFFUSION

Experimentally, the D_p barodiffusion coefficient can be determined by the method using suction of the liquid through a layer of granular material under isothermal conditions [3]. The method is based on replacing capillary barodiffusion with diffusion in an external force field by sucking the liquid through a gypsum frit having a defined resistivity. It is assumed that the same volume flow of liquid results when the pressure gradient of the external force field is identical with the pressure gradient of capillary suction.

At unidirectional flow of liquid due to suction the volume flow is given by the equation

$$h = -D \delta_x C - D_p \delta_x p. \quad (1)$$

If the initial and boundary conditions having the form

$$\begin{array}{llll} t = 0 & x \in (0; h) & C = C_0 & p = p_0 + \rho g(h - x) \\ t > 0 & x = 0 & h = h(t) & p = p_1 \end{array} \quad (2)$$

$$\begin{array}{llll} & x = L(t) & C = C_k & p(L) = p_2 \\ & x = h & C = C_0 & \delta_x C = 0 \end{array} \quad (3)$$

are met, then when knowing C_k and D one can calculate D_p from equation (1).

EXPERIMENTAL RESULTS

The barodiffusion coefficient was measured on an aqueous suspension of $\alpha\text{-Al}_2\text{O}_3$ with particle sizes over the range $(0.1 \mu\text{m}; 0.4 \mu\text{m})$.

The arrangement of the method for measuring the barodiffusion coefficient in a system with an unsaturated boundary is illustrated in Fig. 1.

The vacuum pump with a surge pressure vessel creates pressure p_1 in the space below the frit, permeable solely for the liquid phase. The surge pressure vessel

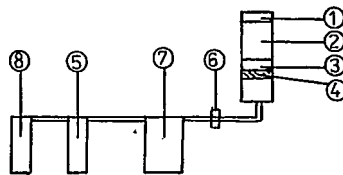


Fig. 1. Method for determining the barodiffusion coefficient.

1 – graduated cylinder, 2 – suspension (slip), 3 – body, 4 – frit, 5 – manometer, 6 – cock, 7 – pressure surge vessel, 8 – vacuum pump

with a capacity larger ten times than the space below the frit allows the required pressure in the system to be attained very quickly. The pressure above the frit is given by the ambient pressure jointly with the hydrostatic pressure produced by the column of liquid in the graduated cylinder. By measuring the liquid phase alone it is possible to determine the resistivity or pressure loss Δp on the frit when knowing the flow rate, density, the sectional area and the difference in height. The resistivity of the frit can also be established by reading the height of water column above the frit at which the water starts to flow through. In the given case the following holds for the pressure above the frit:

$$p_2 = p_0 + \rho gh, \quad (4)$$

where p_0 is the pressure on the liquid surface, ρ is the density of water, h is the column height and g is gravity. If pressure p_0 is also below the frit, i.e. $p_1 = p_0$, then the following holds for the pressure loss on frit having thickness H :

$$\Delta p_f = \rho gh. \quad (5)$$

Knowledge of Δp_f allows Δp on the arising body to be expressed. For the body surface in contact with the suspension also holds equation (4) with the difference that ρ signifies the density of the suspension. The pressure below the frit is measured directly. The pressure difference at the arising body is given by the difference between pressures p_2 and p_1 after subtracting the pressure difference at the frit. For the pressure difference at the frit it then hold that

$$\Delta p_s = p_0 + \rho gh - p_1 - \Delta p_f. \quad (6)$$

The pressure difference at the body varies in terms of time with respect to the change in body thickness in the course of the measurement.

The arrangement of the method allows the time dependence of the volume flow of the liquid, the thickness of the arising body on the frit at a constant p_1 and p_2 to be measured during the experiment with the

Table II

The values of barodiffusion coefficients calculated from equation (7)

t [s]	Δp_s [Pa]	$L \times 10^3$ [m]	D_p [m ⁻² s ⁻¹ Pa ⁻¹]	$\bar{D}_p$ [m ⁻² s ⁻¹ Pa ⁻¹]
10	80000	0.2	3.0×10^{-13}	2.9×10^{-13}
30	80000	1.0	2.9×10^{-13}	
10	70000	0.2	3.0×10^{-13}	
30	70000	0.9	2.7×10^{-13}	

suspension. By measuring C_s on the body-frit boundary at time t while knowing the values of coagulation concentration C_k and the diffusion coefficient, and on using the assumption of a linear concentration profile in the body, it is possible to calculate the barodiffusion coefficient from equation (1).

If the duration of the experiment is short, so that the thickness of the body formed is small, the concentration in the body approaches the coagulation concentration C_k , and the concentration gradient in the body can be neglected. In the given case, equation (1) acquires the form

$$h = -D_p dp/dx. \quad (7)$$

Typical experimentally established relationships $h = h(t)$ and $L = L(t)$ are plotted in Figs. 2 and 3 for $p_1 = 14\,700$ Pa and $p_1 = 20\,000$ Pa. Relations of similar character were also determined for $p_1 = 1\,000$ Pa; $11\,000$ Pa; $30\,400$ Pa. A survey of barodiffusion coefficients D_p calculated according to equation (1) and for $C_k = 0.425$ m³m⁻² and $D = 2.45 \times 10^{-8}$ m²s⁻¹ are listed in Table I.

For short experimental times, the values of D_p were calculated from equation (7) and are listed in Table II.

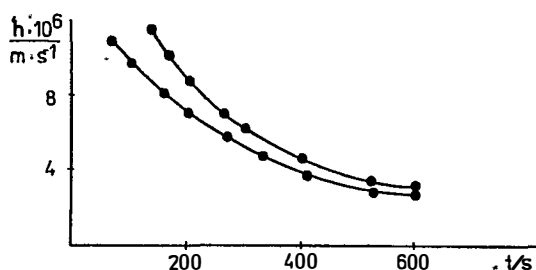


Fig. 2. Time dependence of the volume flow of liquid.
1 - $p_1 = 14\,700$ Pa, 2 - $p_1 = 20\,000$ Pa

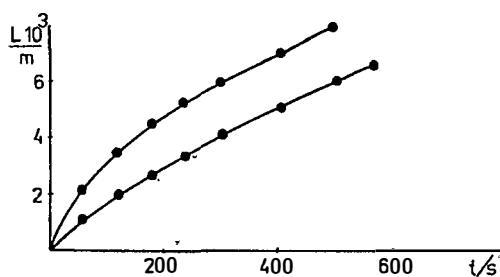


Fig. 3. Time dependence of the body thickness.
1 - $p_1 = 14\,700$ Pa, 2 - $p_1 = 20\,000$ Pa

Table I

The values of diffusion coefficients calculated from equation (1)

t [s]	Δp_s [Pa]	C_s [m ³ m ⁻³]	$L \times 10^3$ [m]	D_p [m ⁻² s ⁻¹ Pa ⁻¹]	$\bar{D}_p$ [m ⁻² s ⁻¹ Pa ⁻¹]
10	80000	0.415	0.2	3.0×10^{-13}	3.0×10^{-13}
30	80000	0.38	1.0	3.1×10^{-13}	
10	70000	0.41	0.2	3.0×10^{-13}	
30	70000	0.38	0.9	2.9×10^{-13}	

CONCLUSION

The measurements indicate that the barodiffusion coefficient is independent of pressure over the range p_1 (1000 Pa; 31000 Pa) and its mean value is $D_p = 3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$. A comparison of the results in Tables I and II shows that the assumption that the concentration gradient in the body is negligible for short durations of the experiment was justified, as virtually identical values of D_p were obtained from both procedures.

The results of the measurements allow the dependence of the volume flow of liquid on the pressure gradient in the body to be expressed as shown in Fig. 4.

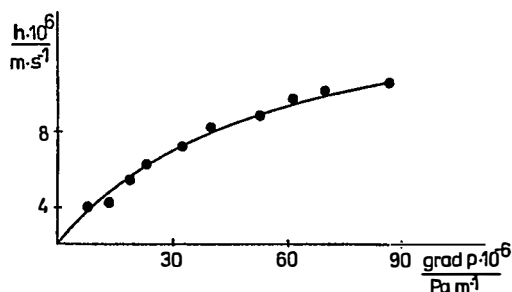


Fig. 4. Dependence of the volume flow of liquid on the pressure gradient in the body.

In the given method, the respective Δp_s is expressed by the external force field, i.e. the vacuum pump. On pouring the suspension, the Δp is produced by the porous mould. If one knows h and L in terms of time on pouring, the relationship in Fig. 4 allows to establish what p_s is produced by the porous form. This finding then makes it possible to characterize quantitatively the suction properties of the given porous mould.

The values of D_p , D and D_{ef} were determined by independent methods. The reliability of the values obtained can be verified by means of equation (1).

For $dC/dx = -32.5 \text{ m}^2 \text{ m}^{-4}$, $dp/dx = 2.25 \times 10^7 \text{ Pa m}^{-1}$, $D = 2.45 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ and $D_p = 3.0 \times 10^{-4} \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$, one obtains the value $h = -7.5 \times 10^{-8} \text{ ms}^{-1}$. At the same time, it also holds for h :

$$h = -D_{ef} dC/dx. \quad (8)$$

For the given values, one then calculates, from equation (8), the value $D_{ef} = 2.3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, virtually identical with the experimentally established D_{ef} ($D_{ef} = 2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$; [8]). The agreement provides evidence for the suitability of methods used in the determination of D , D_p and D_{ef} , as well as that for the determination of C_k , because its knowledge provides the basis for calculating the above material quantities.

References

- [1] Kováč M., Havrda J. *Ceramics-Silikáty* 36, 129 (1992).
- [2] Kováč M., Havrda J.: *Ceramics-Silikáty* 36, 135 (1992).
- [3] Havrda J., Oujř F., Šebšajevič G.: *Silikáty* 28, 311 (1984).

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METODA URČENÍ BARODIFÚZNÍHO KOEFICIENTU KAPALINY V KERAMICKÉ SUSPENZI POPISUJÍCÍHO JEJÍ CHOVÁNÍ PŘI LITÍ DO PORÉZNÍ FORMY

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Byl sledován vliv gradientu tlaku na přenos kapaliny keramickou směsí při lití suspenze do porézní formy. Pro stanovení barodifúzního koeficientu byla vypracována metoda založená na prosávání kapaliny vrstvou porézního materiálu, kde suspenze na fritě je vystavena účinku tlakového rozdílu. Bylo zjištěno, že barodifúzní koeficient

nezávisí na tlaku v rozmezí p_1 (1000 Pa; 31000 Pa) a jeho hodnota pro barodifúzi vody v suspenzi $\alpha\text{-Al}_2\text{O}_3$ je $3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$.

Obr. 1. Metoda stanovení barodifúzního koeficientu.

1 – odměrný válec, 2 – suspenze, 3 – střep, 4 – frita, 5 – manometr, 6 – kohout, 7 – vyrovnávací tlaková nádoba, 8 – vývěva.

Obr. 2. Závislost objemového toku kapaliny na čase.

1 – $p_1 = 14700 \text{ Pa}$, 2 – $p_1 = 20000 \text{ Pa}$

Obr. 3. Závislost tloušťky střepu na čase.

1 – $p_1 = 14700 \text{ Pa}$, 2 – $p_1 = 20000 \text{ Pa}$

Obr. 4. Závislost objemového toku kapaliny na gradientu tlaku ve střepu.

Book Review

HIGH PERFORMANCE CERAMIC FILMS AND COATINGS. Proceedings of Satellite Symposium 1, 7th CIMTEC World Ceramics Congress, Montecatini Terme, Italy, 27–30 June, 1990. Edited by P. Vincenzini, Faenza, Italy, 1991, 756 pages. Price: US \$ 214.50/Dfl. 430.00

The contributions in this volume concentrate on recent progress in CVD, PVD, thermal spraying, epitaxial growth, sol/gel and related techniques used to deposit monolayer, multilayer, composite, hybrid and multifunctional ceramic thin/thick films and coatings on metal and ceramic substrates. The 71 papers, including 9 invited, report on the results of studies on the characterization of structural and functional properties of materials for a number of applications such as wear, erosion, corrosion, thermal protection, and uses in electronic, magnetic, optical and opto-electronic devices.

Contents:

SECTION 1: MATERIALS ELABORATION AND COATING TECHNIQUES

1.1. Thermal Spraying

Modelling of plasma spraying of ceramic coatings at atmospheric pressure (Invited Lecture)

Characterization of tungsten carbide coatings as a function of powder manufacturing and deposition technologies

Advanced ceramic powders for thermal spray coatings and monolithic ceramics

Plasma spray deposition of alumina-based ceramic coatings

HIP treatment for ZrO_2 coating prepared by low pressure plasma spraying

YSZ powders (ZIRCYT) for plasma spraying

1.2. CVD/PVD Coatings

Vapor deposited ceramic coating: status and prospect (Invited Lecture)

Thin ceramic films deposited by ion beams (Invited Lecture)

Synthesis of tailored thin films of oxide superconductors by excimer laser ablation (Invited Lecture)

Modelling of pulse CVI using a fine SiO_2 tube sealed at an end

Epitaxial growth of YIG films on GGG single crystal with an alkoxide method

Kinetics of deposition of zirconia-based ceramics from $\text{ZrCl}_4\text{-H}_2\text{-CO}_2\text{-Ar}$ gas mixtures

Deposition kinetics of CVD TiO_2

Ceramic epitaxial films and multilayers prepared by MOCVD

Formation and properties of titanium nitride layers produced under glow discharge conditions

Formation of titanium nitride layers from a gaseous phase with the participation of a chemical reaction

Preparation of a-C:H films by ion-assisted methods

1.3. Sol/Gel and Miscellaneous Coating Techniques

Protective coatings for organic polymers by sol-gel techniques

Realisation at room temperature of adhesive amorphous silica coating on bare ferrous surfaces

Anodic spark deposition – A novel approach to ceramic coatings

Preparation and properties of thin TiO_2 - and $\text{TiO}_2/\text{V}_2\text{O}_5$ -coatings by a sol-gel method

Preparation and properties of In_2O_3 thin films by the sol-gel method

Phase characterization of gel products containing SiO_2 and SnO_2

Fe(III) containing gel products and their spectroscopy characteristics

SECTION 2: CHARACTERIZATION OF COATINGS AND FILMS

2.1. Thermal Sprayed Coatings

Elastic anisotropy of APS alumina coatings and its relationship to microstructure (Invited Lecture)

Characterization of the interface between partially stabilized zirconia thermal barrier coatings and the NiCrAlY bond coat

Analysis and calibration a shear fracture toughness test for thermally sprayed coatings