

Influence of Structure of Skeleton Materials on Permeability of Liquids

Vytenis ZABUKAS*, Valdas KVEDARAS, Tatjana PAULAUSKIENĖ

Department of Technological Processes, Klaipėda University, Bijūnų 17, LT-91225 Klaipėda, Lithuania

Received 04 July 2008; accepted 26 February 2009

Permeability of various liquids in pores of skeleton materials (porous samples from powders of reduced iron and alloy steel Cr-Ni-Ti, porous ceramic ZrO_2/CaO and carbonisates of polyvinyl alcohol) is analysed. It is shown, that at the flow of liquid monomers through ceramic and metal porous materials the flow rate depends on pressure difference rectilinearly. Such rectilinear dependence is absent at the flow of liquids of high viscosity (for example, solutions of polymers) through skeleton materials with fine pores (diameter of pores $< 50\ \mu m - 60\ \mu m$). During the research of permeability of low viscosity liquids in porous capillaries with the diameter less than $100\ \mu m$, an effect of obliteration is found. This effect is caused by adsorption processes in boundary layers and increase of viscosity of part of a liquid interacting with solid surface. Analysis of processes of permeability of styrene, methyl methacrylate (MMA) in porous media with high activity of a surface (carbonaceous polymer) has shown that the development of obliteration is promoted by more developed fine porosity, tortuosity of pores and increase of the rate of flow of a liquid phase (pressure difference). Various functional groups formed on the surface of pores of carbonisate interact with molecules of liquids (monomers) and form intermediate buffer layers of by-products of reaction. Formation of such buffer layers changes resistance of skeleton system to permeability of a liquid phase and, thus, promotes development of effect of obliteration.

Keywords: skeleton materials, obliteration, permeability, porous metals, ceramic, carbonaceous polymer.

1. INTRODUCTION

For the time being, composite materials in the structure including porous skeleton materials and the polymeric components introduced in porous media get wide application [1, 2]. In these composites polymeric phase provides functions of strengthening and heat-shielding at impact of mechanical and heating factors on material. Therefore such composite materials can be successfully used in conditions of intensive heat-mass transfer in various power systems. To produce such composite materials various skeleton materials can be used: porous metals (materials from Fe, Al, alloy steel and etc. powders), ceramics (ZrO_2 , Al_2O_3 , MgO and etc.) and carbonaceous polymers (polyvinyl alcohol (PVA), polyacrylonitrile, derivatives of cellulose and etc.) [3–7]. At formation of composite materials of the system “a skeleton component – polymer”, there are limited possibilities to change the structure of a phase: the amount of a skeleton component is constant, and the amount of a polymer in pores of a skeleton material is limited by the open porosity.

Various solutions and melts of polymers for filling porous space of a skeleton material with polymers are used. However, as polymeric solutions and melts, in particular, have high viscosity, filling of pores of a skeleton component with them is technically complicated. Thus only a low degree of filling of pores of a skeleton component is available. Full filling of pores can only be reached, when the thickness of porous metal covering does not exceed $0.3\ mm$ at introduction melts of polymers. Progressive production method of composite materials of system “a skeleton material – polymer” is filling pores of skeleton materials with liquid monomers (for example,

MMA, styrene) with their subsequent polymerisation in pores of a skeleton material [8, 9].

The properties of the composite materials of the system “a skeleton material – polymer”, formed by filling pores of a skeleton component with polymers or their compositions, are appreciably caused by phase interaction of the components [10, 11]. During formation of composite materials of the system “a skeleton material – polymer” diffusion processes are accompanied by chemical reactions on the interface of phases [12]. However, up till now questions regarding the studies the interphase phenomena at filling porous space of various skeleton materials with liquids, in particular, monomers were only little mentioned by researchers.

The purpose of the present work is to investigate the features of permeation of various liquids in porous space of skeleton materials (porous iron and alloy steel, ceramic ZrO_2/CaO , carbonaceous PVA) as well as to estimate influence of porous structure of a skeleton material and interphase interaction on the flow rate and degree of filling porous space with liquids.

2. EXPERIMENTAL

Materials with the developed porous structure were used in the research: metal, ceramic and carbon (polymeric carbonisates) (Fig. 1).

Metal skeleton samples have been produced from the reduced iron (ИДКБ-3 by GOST) (Fig. 1, a) and the alloyed steel Cr-Ni-Ti (18 % Cr, 9 % Ni, 1 % Ti, ИРХ18Н9Т by GOST) powders by a method of hydrostatic pressing and sintering. The samples were made $25\ mm$ in diameter and $8\ mm - 10\ mm$ in height in this way. Two types of metal particles were used for the sampling: $125\ \mu m - 160\ \mu m$ and $56\ \mu m - 63\ \mu m$. Metal particles were of spherical or plate forms. Open porosity of metal skeleton samples changed within the range of 20 %–30 %.

*Corresponding author. Tel.: +370-46-398696; fax: +370-46-398682.
E-mail address: tpk.jtf@ku.lt (V. Zabukas)

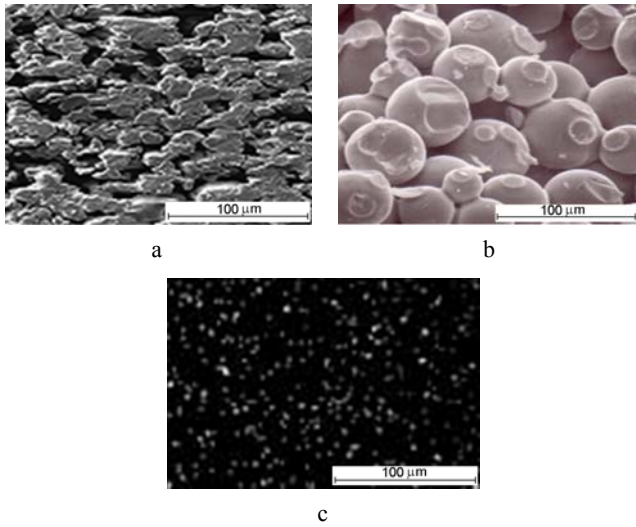


Fig. 1. The general view of the materials with developed porous structure: a – metal sample produced from plate form particles of reduced iron; b – the ceramic sample sintered from micro spheres ZrO_2/CaO ; c – the sample of the carbonaceous thermooxidized polyvinyl alcohol (PVA)

Ceramic skeleton samples were produced from zirconium dioxide powders modified with calcium oxide (ZrO_2/CaO) by a method of hydrostatic pressing and sintering (Fig. 1, b). The samples were produced from the following types of spherical particles: $20\ \mu\text{m}$ – $40\ \mu\text{m}$, $56\ \mu\text{m}$ – $63\ \mu\text{m}$ and $90\ \mu\text{m}$ – $100\ \mu\text{m}$. Open porosity of the ZrO_2/CaO samples changed within the range of 30 %–40 %.

Polymeric carbonisates were also used as a skeleton material (Fig. 1, c). Polymeric carbonisates were produced by heating at $900\ ^\circ\text{C}$ – $1000\ ^\circ\text{C}$ in the inert gas (nitrogen) of PVA thermooxidized at $190\ ^\circ\text{C}$. For activation of carbonisation, PVA was preliminary treated with 1 %–10 % water solutions of lithium chloride (LiCl).

Permeability of liquids through the samples specified here in above and the mentioned skeleton materials were investigated applying water, ethyl alcohol, styrene and methyl methacrylate (MMA).

Porosity, size of the open pores, was measured in various skeleton materials by using a method of replacement of a liquid from pores. This method allows filling the porous spaces fully with corresponding moistening liquid and its subsequent replacement from pores with gases, measuring its pressure. The principle scheme of device for definition of the sizes of pores by a method of replacement of a liquid from pores is represented in Fig. 2.

The porous sample in diameter of 25 mm and 8 mm of height was fully impregnated with a liquid. After exposure in a liquid not less than 12 hours, the impregnated porous sample was located in a special hermetic tubular holder. The top surface of the sample was filled up with a thin layer of a liquid (up to 3 mm). From the other end face of the sample the pressure is raised smoothly ($10\ \text{Pa/s}$). The pressure is created by means of compressed air of the holder submitted to the bottom of the device. During that moment, when the first series of air bubbles came off from the top of the surface, indication of a manometer 8 was fixed. This value by a manometer allows to calculate the maximum diameter of pores. Further on, the pressure

raises up to value, at which intensive bubbling on the entire surface of the sample begins. The value of this pressure allows to calculate the average diameter of the pores.

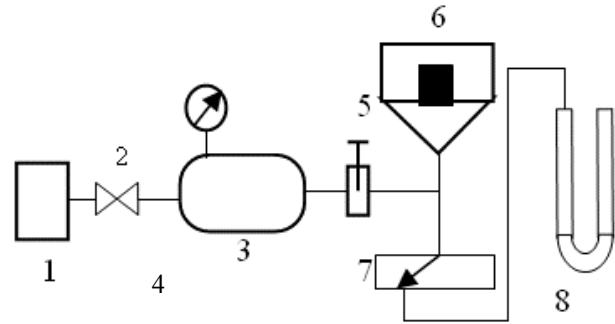


Fig. 2. The scheme of device of measuring of the sizes of pores by method of replacement of a liquid from pores: 1 – compressor; 2 – valve; 3 – pressure chamber; 4 – manometer; 5 – smooth regulator of pressure in system of replacement of a liquid; 6 – holder of the sample; 7 – discrete divider of pressure; 8 – U-manometer

This device was used for research of permeability of various liquids in skeleton materials.

3. RESULTS AND DISCUSSION

At one-dimensional flow of a liquid in pores of a skeleton material, the distribution of the pressure in a direction of a flow of a liquid can be expressed as follows [13]:

$$dp = \left(\lambda \frac{h}{d_{\Pi}} + \xi \right) \frac{\rho V^2}{2} dx, \quad (1)$$

where: λ is the factor of friction; ξ is the factor of hydraulic resistance; h and d_{Π} – respectively, the length and the diameter of the pores; V is the average rate of a flow of a liquid; ρ is the density of a liquid.

However, it is necessary to note that this dependence is valid only at presence of pores of large-scale sizes, i. e. with diameter over $100\ \mu\text{m}$. In the case of flow of a liquid through capillaries of smaller sizes, a change in the rate of its flow at various stages of the process is observed. Our investigations indicated that at the permeation liquids through materials with fine porosity it is possible to distinguish four subsequent stages of the flow (Fig. 3): I – stage of increase in the rate; II – stage of transition to decrease in the rate; III – stage of downturn of the rate, and IV – stage of the flow of a liquid with a constant rate.

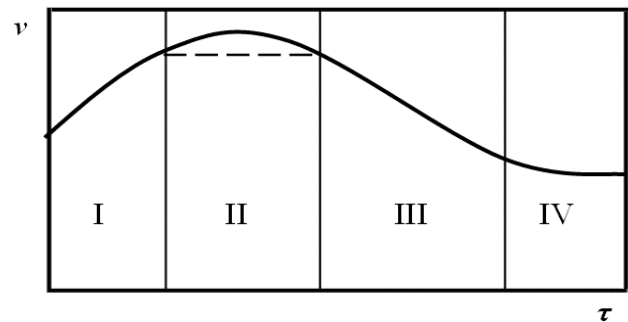


Fig. 3. The scheme of the change of the volumetric flow rate (v) of a liquid through a porous material during a certain period of time (τ)

The first stage is rather short. It is more expressed at permeation of monomers (for example, styrene and MMA) through porous metals (Fig. 4). Increase of the rate of permeation of a liquid at the first stage shows the occurrence and development processes of adsorption and formation of a boundary layer. Duration of this stage depends on the size and the form of samples, the size and geometry of the porous space in a skeleton material. The increase in the rate of permeation of MMA in pores of alloy steel Cr-Ni-Ti, produced from spherical particles, is observed in the samples with fine-scale pores and the expressed specific surface of the pores (Fig. 4).

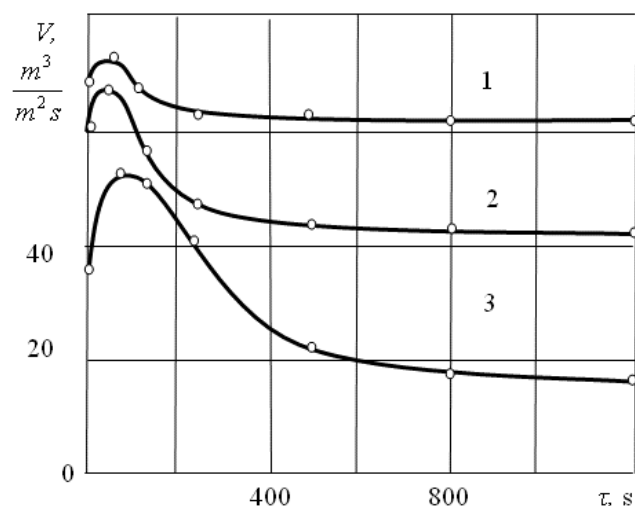


Fig. 4. Kinetics of the volumetric flow rate (v) of MMA proceeding through a porous alloy steel Cr-Ni-Ti layer (2 mm) produced from spherical particles of different porosity, diameter of particles (fraction) and a specific surface of pores: 1 – 0.265, 125...160 μm ; $3.09 \cdot 10^4 \text{ m}^2/\text{m}^3$; 2 – 0.192, 56...63 μm ; $8.14 \cdot 10^4 \text{ m}^2/\text{m}^3$; 3 – 0.19, 40...56 μm ; $9.96 \cdot 10^4 \text{ m}^2/\text{m}^3$

It can be seen that duration of the first stage increases with increase of the specific surface of the pores in a material. It is possible to explain the increase in the flow rate of a liquid in the initial stage by the action of forces of molecular interaction, which arises on interface between the liquid and solid phases [12, 14]. When filling a porous body with a liquid, the direction of the tension, acting on the formation of a boundary interphase layer, coincides with a direction of the external pressure Δp . In our opinion, it is the main reason causing the acceleration of a liquid permeation. The effect of initial acceleration is mostly expressed at permeation of liquid monomers in porous carbonaceous bodies, and the least expressed in the ceramic materials possessing low potential characteristics of the surface (Fig. 5).

Duration of this period depends not only on the structure and the kind of a porous material, but also on the size of the skeleton sample. This period comes to the end of formation of a boundary layer at interaction between liquid and solid phases. At this stage, the spaces that have formed between the boundary layers are filled.

It comes to the end with the beginning of the outflow of a liquid from the porous sample. If at the first stage the direction of the forces of interphase action coincides with the direction of the enclosed pressure, so at the third stage the force of interphase action impedes the outflow of a

liquid from the porous sample. The volumetric flow rate (v) of a liquid starts to decrease from this moment on. It testifies the presence of the same phenomena of adsorption in the generated boundary layers reducing “alive” section of porous channels of the material [15].

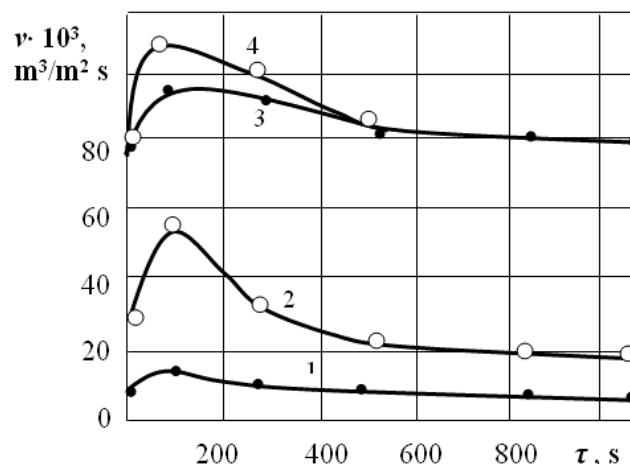


Fig. 5. Kinetics of the volumetric flow rate (v) of MMA-proceeding through porous layers (2 mm) from: 1 – ceramics Al_2O_3 ($I_0 = 0.19$, $d_{II} = 28 \mu\text{m}$); 2 – porous alloy steel Cr-Ni-Ti ($I_0 = 0.19$, $d_{II} = 28 \mu\text{m}$); 3 – carbonaceous PVA ($I_0 = 0.194$, $d_{II} = 28 \mu\text{m}$) and 4 – carbonaceous PVA at presence 10 % LiCl ($I_0 = 0.195$, $d_{II} = 32.3 \mu\text{m}$)

The arisen so-called obliteration is caused by the increase of viscosity of that part of a liquid, which is in a field of action of a surface of a solid phase. It is known that viscosity of a liquid in capillaries can rise by up to three times in comparison with viscosity of a liquid in a free condition [13]. It can be the main reason causing the stopping of liquid permeation in the porous space. The main causes of the obliteration are forces of molecular and electric interaction between the phases. They are sources of formation on a surface of pores of the adsorbed layers of the polarly-active molecules reducing “alive” cross-section of a porous capillary. These adsorbed layers in each material are in a non-equilibrium condition. Therefore, the field of molecular interactions is in an unbalanced condition. It reduces a power barrier of interaction of liquid and solid phases. Usually researchers increase the rate of flow through porous materials by increasing the temperature to explain the viscosity of the liquid [14, 15]. However, in this case the main role is played by the increased intensity of the thermal movement of molecules of a liquid in porous space. This reduces thickness of a boundary layer and increases “alive” section of porous channels. The results received at the research of permeation of the styrene through the porous alloy steel Cr-Ni-Ti with high activity of the surface pores serve for the favour of the reasoning. It is established, that a great influence on obliteration renders the structure of a porous material. Development of fine-scale porosity and tortuosity of pores strengthens effect of obliteration (Fig. 6). In this case, decrease in the rate of flow of styrene through the porous metal samples received from Cr-Ni-Ti powders of finer-scale fraction is observed. In this case decrease in the volumetric flow rate (v) of styrene is observed for the porous alloy steel samples received from the particles of finer-scale fraction.

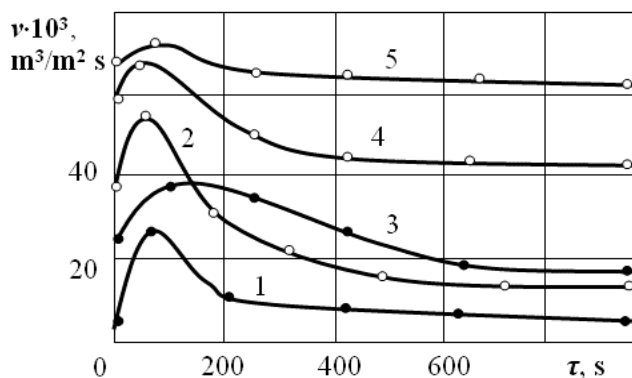


Fig. 6. Kinetics of the volumetric flow rate (v) of the styrene proceeding through the porous a layer ($h = 2$ mm) of porous alloy steel Cr-Ni-Ti made from spherical (2–5) or plate form particles of reduced iron (1) different factions: 40...56 μm (1, 2, 3); 56...63 μm (4); 125...160 μm (5) at room (1, 2, 4, 5) or raised (40 °C) (3) temperatures

The effect of obliteration is more pronounced, when plate form particles are used for the manufacturing of porous metal samples. Such materials have raised tortuosity of pores. Except for phenomena analysed hereinabove, the obliteration is increased by polymerisation of monomers in pores of a skeleton material. Formed oligomers raising viscosity of a liquid phase can considerably slow down or even discontinue the flow processes. Those phenomena are undesirable at impregnation of skeleton materials during formation of composite materials of the system “a skeleton material – polymer”. Therefore, it is necessary to create such technological conditions that polymerisation would begin only after filling all porous space of a skeleton material with a monomer. It was established, that the value of the pressure difference and, subsequently, the rate of permeation of liquids influences processes of obliteration (Fig. 7).

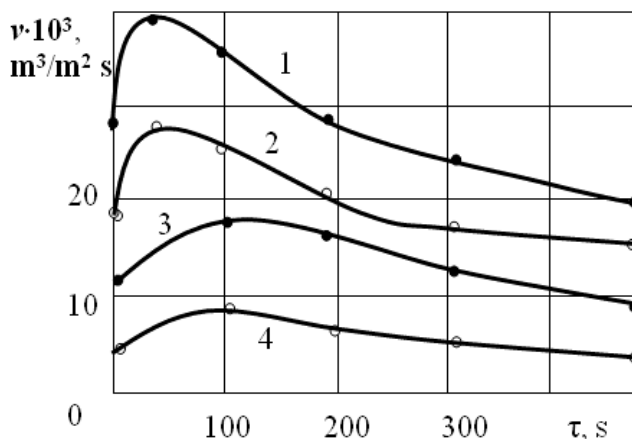


Fig. 7. Kinetics of the volumetric flow rate (v) of the styrene proceeding through the porous layer ($\Pi_0 = 0.39$) of ceramics ($h = 10$ mm) made from spherical particles ZrO_2/CaO . Faction 90...100 μm . Pressure differences (MPa): 1 – 0.05; 2 – 0.035; 3 – 0.025; 4 – 0.015

As seen from the presented data, the increase in the pressure difference of a liquid (styrene) at its permeation through the porous ceramics received by sintering of spherical particles ZrO_2/CaO strengthens the effect of obliteration. It is necessary to consider that the reason of the increased obliteration subsists at increasing the

volumetric flow rate (v) of a liquid in pores of a skeleton material and changing the character of the flow of a liquid. Here we can have laminar or turbulent kind of flow of a liquid phase.

Such assumption cannot be lead by making up the equations of criteria. Porous media geometrically are too complicated to be presented by elementary cylindrical channels. There are many curvatures, ledges of a surface, roughness, etc. in each porous material. All these factors promote local turbulence in pores of a skeleton material and raise internal resistance of a sample to the enclosed pressure. The carried out research reveals that obliteration, irrespective of the reasons of its occurrence, leads to increase in hydraulic resistance of materials of fine-scale porosity. In [7] it is shown that the effect of obliteration is absent in materials of large-scale porosity ($d_H > 40$ μm). However, we consider that in practice these effects are real for each porous material, as there are pores of various diameters in each one of them. Kinetic dependences of permeation liquids through the skeleton materials can be analytically presented in the form of the equation:

$$\frac{v}{v_{\max}} = 1 - K(1 - e^{-\frac{\tau - \tau_2}{\tau_3 - \tau_2}}), \quad (2)$$

where v is the volumetric flow rate of a liquid at a certain moment τ during the period of obliteration $\tau_2 - \tau_3$, $\text{m}^3/\text{m}^2\text{s}$; $v_{\max}$ is the volumetric flow rate of a liquid at the moment of time $\tau = \tau_2$, $\text{m}^3/\text{m}^2\text{s}$; K is the dimensionless factor, describing reduction of the relative volumetric flow rate ($v/v_{\max}$) of a liquid during obliteration; $\tau_3 - \tau_2$ is the time interval of the course of obliteration (τ_2 – beginning, τ_3 – end), s.

The values of factors K and the time period of obliteration $\tau_3 - \tau_2$ on experimental dependences $v = f(\tau)$ (Fig. 4–5) are shown in the Tables 1–3. First of all, we shall analyse the basic characteristics of permeation of liquids into porous metals (Table 1). As can be seen from the presented results, the nature of the liquid makes essential impact on the change of the factor K in the equation (2). For example, comparing the value K for various liquids (the skeleton material from spherical particles of the reduced iron, faction 125 μm – 160 μm , the open porosity 22 %) with certain K values, it is possible to set them out in the following sequence:

$$K_{\text{H}_2\text{O}} > K_{\text{C}_2\text{H}_5\text{OH}} > K_{\text{styrene}} > K_{\text{MMA}}. \quad (3)$$

When trying to explain the essence of obliteration from the point of view of action of an electrostatic field of metal pores on molecules of a liquid, it follows that orientation of molecules of a liquid on the surface of pores will occur easier with the increase of the dipole moment of molecules of a liquid. Such assumption allows making a conclusion that obliteration will be more expressed with higher dipole moment of molecules of liquid, i. e.:

$$\mu_{\text{H}_2\text{O}} > \mu_{\text{C}_2\text{H}_5\text{OH}} > \mu_{\text{styrene}} > \mu_{\text{MMA}}. \quad (4)$$

It is difficult to define experimentally influence of the nature of porous metal on permeability of a liquid. These difficulties arise, as it is practically impossible to create identical porous structures at manufacturing the samples of metals. For example, if the investigated samples of porous

metals, made from spherical particles of alloy steel Cr-Ni-Ti or reduced iron of faction 125 μm –160 μm have approximately identical average diameter of pores, their open porosity, however, will differ under such characteristics, as well as the distribution of pores in the sizes, tortuosity, a roughness of a surface, etc. Research of permeation of various monomers through the porous metals has shown that intensity of obliteration is approximately identical: the established values of factor K in the equation (2) are almost equal (0.22 and 0.20) (Table 1). The relative volumetric flow rate (v/v_{max}) of a liquid decreases with reduction factor K and increases with reduction of the diameter of pores of metal. It is shown, that intensity of obliteration of water depends not only on the structure of the porous metal, but also on the volumetric flow rate of water in the pores: the higher is the rate of water in the pores, the more intensive the process of obliteration is.

It is necessary to note, that tortuosity of pores, a curvature of pores on length, various expansions, the developed roughness of the surface of pores, i.e. all the structural factors increasing a specific surface of pores promote the increase of the factor K . It is obvious from comparison of the results received during the research of permeation of styrene through porous metal samples from the particles of spherical and plate forms of identical

factions (Table 1, positions 6 and 8). With increase in the sizes of particles (faction) ZrO_2/CaO , from which porous ceramic samples were made, the effect of obliteration is less expressed (Table 2). For example, at increase in sizes of particles from 20 μm –40 μm to up to 90 μm –100 μm , the factor K in the equation (2) decreases from 0.16 to up to 0.10. If to compare these values of the factor K with the values of the factor K determined in tests with the metal samples in identical external and structural conditions, it can be seen that they are lowered. Decrease in factor K indicates reduction in activity of a surface and intensity of diffusion processes. Studies of laws of diffusion show that the energy of activation of diffusion processes of metal atoms above, than energy of activation for non-metallic atoms.

On the other hand, it is also necessary to consider different structural formations in these materials. The crystal lattice of oxides is very complex and contains many defects. According to the “hole” theory [16], these defects promote development of diffusion processes and formation of a boundary layer. However, it is impossible to oppose the factor promoting phase interaction with this diffusion factor, and, therefore, the processes of obliteration. Introduction of molecules of a liquid in defective places of crystal structure should be considered as formation of the buffer liquid layers reducing friction between the surface

Table 1. Basic characteristics of process of the flow of various liquids through porous samples (thickness of 8 mm) made from metal powders by method of hydrostatic pressing and sintering

No	Porous sample from metal powders	Form of particles	Faction, μm	Average diameter of pores, μm	Open porosity, %	Liquid	Value of pressure difference, $\Delta p/h \cdot 10^{-5}$, Pa/m	Values of constants in the equation (2)		
								K	τ_2 , s	τ_3 , s
1	Reduced iron	Spherical	125–160	40	22	Styrene	100	0.22	60	200
2			56–63	16	20			0.29	120	420
3			125–160	40	22	MMA		0.20	30	180
4						Water		0.37	150	450
5						$\text{C}_2\text{H}_5\text{OH}$		0.28	90	300
6	Alloy steel Cr-Ni-Ti	Spherical	125–160	45	27	Styrene	120	0.20	0–30	180
7						$\text{C}_2\text{H}_5\text{OH}$		0.24	60	300
8		Plate		30	20	Styrene		0.31	210	420

Table 2. Basic characteristics of process of the flow of various liquids through porous ZrO_2/CaO ceramic samples (thickness of 10 mm)

No	Porous ceramic	Form of particles	Faction, μm	Average diameter of pores, μm	Open porosity, %	Liquid	Value of pressure difference, $\Delta p/h \cdot 10^{-5}$, Pa/m	Values of constants on the equation (2)		
								K	τ_2 , s	τ_3 , s
1	ZrO_2/CaO	Spherical	20–40	9.4	32	Styrene	100	0.16	120	300
2			56–63	9.4	34			0.13	60	240
3			90–100	40.5	40			0.10	0–30	180
4			90–100	40.5	40	MMA		0.15	0–30	210
5			90–100	40.5	40	Water		0.37	210	480
6			90–100	40.5	40	$\text{C}_2\text{H}_5\text{OH}$		0.17	120	380

Table 3. Basic characteristics of process of the flow of various liquids through porous samples (thickness of 10 mm) made from carbonisates of various modifications PVA

No	Carbonisate of PVA modification	Open porosity, %	Average diameter of pores, μm	Liquid	Values of constants in the equation (2)			Value of pressure difference, $\Delta p/h \cdot 10^{-5}$, Pa/m
					K	τ_2 , s	τ_3 , s	
1	PVA, thermal oxidized	16.6	18	Styrene	0.15	30	240	130
				Water	0.08	0–30	180	
2	PVA, thermal oxidized after processing: 1 % LiCl or 10 % LiCl	7.2	16.2	Styrene	0.14	0	240	
				Water	0.21	30	240	
		19.5	32.3	Water	0.4	0–30	900	
3	Thermal oxidized composition PVA + 3 % PVA fibre MVM-2	7.2	12.2	Styrene	0.27	60	360	

of the pores of a material and a liquid. It is possible to use a hypothesis of formation of adsorption condensed films for the explanation of the mechanism of formation of these interphase layers. In comparison with other liquids, water has the highest activity from the point of view of obliteration in ceramic materials. For example, at permeation of water through ceramics from spherical particles ZrO_2/CaO of monofaction $80\text{ }\mu\text{m} - 100\text{ }\mu\text{m}$, the process is described by the equation (2), in which the factor K reaches high enough value – 0.37. The maximum value K has been established to be equal to 0.42 in experiments with ceramics ZrO_2/CaO of faction $20\text{ }\mu\text{m} - 40\text{ }\mu\text{m}$. It allows explaining the increase of the factor K in the course of chemical adsorption process on the border of phases, i.e. chemical interaction of the molecules of water and the stabilizing additive of the ceramics CaO .

A similar phenomenon is also observed at the research of permeation of water through the porous samples of carbonaceous PVA preliminary processed by LiCl solutions of various concentrations (Table 3). In this case, the residues of crystallites LiCl in carbonaceous material are the strong centre of gravity of molecules of water. As a result of such interaction, $\text{LiCl} \cdot n\text{H}_2\text{O}$ crystal hydrates on the surface of the pores are formed. A similar mechanism of action LiCl from the point of view of molecules of water is discussed at revealing its influence on dehydration of PVA and formation of the conjugated structures in carbonaceous polymer [17, 18].

As can be seen from the data presented in Table 3, permeation of styrene through carbonaceous PVA materials differs by low value of factor K , which indicates poorly expressed obliteration. Effects of obliteration of the flow of styrene are mostly expressed in the carbonaceous materials received from polymeric compositions after thermal oxidizing: PVA and PVA fibres. The reason of it is geometrical complication of the porous spaces in the homogeneously reinforced material. As the carbonaceous material pores are twisting, they often form loops around carbonaceous PVA fibres. Despite of the low open porosity, a material contains many fine-scale pores and, therefore, has a high specific surface of pores.

4. CONCLUSIONS

1. It is established that at the flow of liquid monomers through ceramic and metal porous materials, the flow rate of monomers rectilinearly depends on the pressure difference. Such rectilinear dependence is absent at the permeation of high viscosity liquids (for example, solutions of polymers) through fine pores (diameter of pores $< 50\text{ }\mu\text{m} - 60\text{ }\mu\text{m}$) of skeleton materials.
2. At permeation of liquids of low viscosity through porous capillaries with the diameter less than $100\text{ }\mu\text{m}$, the effect of obliteration is determined. The phenomenon of obliteration is caused by adsorption processes in boundary layers and by increase of viscosity of that part of liquid, which is in a field of action of the surface of the solid phase. Research of permeation of styrene, methyl methacrylate through the pores with high activity of a surface (carbonaceous polymers) indicates that obliteration is promoted by more developed fine-scale porosity, tortuosity of pores, increase in the flow rate of liquids and pressure difference.
3. When filling porous space of skeleton materials with a liquid phase, two kinds of mass-transfer were developed: volumetric diffusion, which is dominant in large-scale pores, and molecular diffusion, which is dominant in fine-scale pores. It is established, that at diffusion interaction of a liquid with a surface of the pores in the boundary layer topographical reactions also proceed. Finally, they are found in the carbonaceous materials. Various functional groups formed on the surface of the pores of carbonaceous material interacting with molecules of liquids (monomers) form intermediate buffer layers of by-products of reaction. Formation of such buffer layers changes the resistance of the skeleton system to permeation of a liquid phase and, thus, promotes development of effect of obliteration.

REFERENCES

1. Kokubo, T., Kim, H.-M., Miyaji, F., Takadama H., Miyazaki, T. Ceramic-Metal and Ceramic-Polymer

- Composites Prepared by Biomimetic Process. Part A. *Applied Science and Manufacturing* 30 (4) April 1999: pp. 405–409.
2. **Paolo Colombo.** Engineering Porosity in Polymer Derived Ceramics *Journal of the European Ceramic Society* 28 (7) 2008: pp. 1389–1395.
 3. **Asthana, R., Kumar, A., Dahotre, N. B.** Powder Metallurgy and Ceramic Forming *Materials Processing and Manufacturing Science* 2006: pp. 167–245.
 4. **Elssner, G., Hoven, H., Kiessler, G., Welliner, P., Wert, R.** Ceramic and Ceramic Composites. Elsevier, 1999: 175 p.
 5. **Guy, A., Montavon, G., Hlawka, F., Cornet, A., Coddet, C.** Microstructure of Partially Stabilized Zirconia Manufactured via Hybrid Plasma Spray Process *Ceramic International* 31 (4) 2005: pp. 611–619.
 6. Carbon Materials for Advanced Technologies. Ed. by **Burchell, T. D.** Elsevier Ltd, 1999: 540 p.
 7. **Lefebvre, J., Mamleev, V., Le Bras, M., Bourbigot, S.** Kinetic Analysis of Pyrolysis of Cross-linked Polymers. *Polymer Degradation and Stability* 88 (1) April 2005: pp. 85–91.
 8. **Zabukas, V., Gvezdauskienė, N.** Effect of Polymer Impregnation on Mechanical Behaviour of Ceramic Materials with a Skeleton of Spherical Particles *Medžiagotyra (Materials Science)* 3 1999: pp. 38–45.
 9. **Zabukas, V., Paulauskienė, T.** Research and Modeling of Porous Structure of Metal Skeleton Materials *Mechanika 2008, Proceedings of the 13th International Conference* April 3–4, 2008: pp. 529–534.
 10. **Ronquerol, F., Ronquerol, J., Sing, K.** Adsorption by Powders and Porous Solids. Elsevier Ltd, 1999: 467 p.
 11. **Boehm, H. P.** Some Aspects of the Surface Chemistry of Carbon Blacks and other Carbon *Carbon* 32 (5) 1994: pp. 759–769.
 12. **Yoshiyuki Endo, Da-Ren Chen, David Y. H. Pui.** Theoretical Consideration of Permeation Resistance of Fluid through a Particle Packed Layer *Powder Technology* 124 (1–2) 8 April 2002: pp. 119–126.
 13. **Belov, S. B.** Porous Metals in Mechanical Engineering. M.: Mechanical Engineering, 1981: 247 p. (in Russian).
 14. **Kannen, K., Rajagopal, R. K.** Flow through Porous Media due to High Pressure Gradients *Applied Mathematics and Computation* 199 (2) June 2008: pp. 748–59.
 15. **Lebon, G., Coot, A.** A Thermodynamical Modelling of Fluids Flows through Porous Media: Application to Natural Convection *International Journal of Heat and Mass Transfer* 29 (3) March 1986: pp. 381–390.
 16. **Carlos Moreno-Castilla.** Adsorption of Organic Molecules from Aqueous Solutions on Carbon Materials *Carbon* 42 (1) 2004: pp. 381–390.
 17. **McNeill, I. C.** Thermal Degradation Mechanisms of Some Addition Polymers and Copolymers *Journal of Analytical and Applied Pyrolysis* 40–41 May 1997: pp. 21–41.
 18. **Zheng Peng, Link Xue Kong.** A Thermal Degradation Mechanism of Polyvinyl Alcohol/Silica Nanocomposites *Polymer Degradation and Stability* 92 (6) June 2007: pp. 1061–107.

*Presented at the 17th International Conference
"Materials Engineering'2008"
(Kaunas, Lithuania, November 06–07, 2008)*