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STUDY OF THE FORMATION OF GAS-VAPOR IN THE LIQUID MIXTURE

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Досліджено процеси формування газо-парової фази в рідких сумішах, які перебувають в стані термодинамічної рівноваги. Визначено термодинамічні параметри газо-парової фази, на основі яких запропонована методика управління інтенсивністю фазового переходу в рідких сумішах зі змінними реологічними властивостями, зокрема в'язкістю і щільністю. Отримано математичні залежності, що використані для аналізу та управління процесами спучування рідких гелеподібних сумішей в технології виробництва пористих матеріалів

Ключові слова: пароутворення, реологія рідких сумішей, термодинамічні параметри парової області

Исследованы процессы формирования газо-паровой фазы в жидких смесях, находящихся в состоянии термодинамического равновесия. Определены термодинамические параметры газо-паровой фазы, на основе которых предложена методика управления интенсивностью фазового перехода в смесях взаимно не растворимых жидкостей с изменяющимися реологическими свойствами, в частности вязкостью и плотностью. Полученные математические зависимости реализованы для анализа и управления процессами вспучивания жидких гелеобразных смесей в технологии производства пористых материалов

Ключевые слова: парообразование, реология жидких смесей, термодинамические параметры паровой области

1. Introduction

Significant part of the modern technological processes of structure formation of materials are based on the thermal impact on various raw mixtures, which implement in them physical and chemical processes that create conditions for structure formation. Such processes can be controlled, but it is necessary to find qualitative and quantitative dependencies of the changing thermal properties of materials in the process of their formation.

Investigation and control of the processes of structure formation of materials are difficult tasks, which are still unsolved. Clear understanding of the mechanism of structure formation makes it possible to develop a methodological basis of new technologies, including the technology of production of thermal insulating materials with predictable thermal properties.

However, the ways of formation of the porous structure are still little investigated, and a clear relationship between the porosity and the physical properties of the material were not found. A lot of experimental data show the relationship between the porosity of the material and its thermal properties [1–3]. It is obvious that the structure of the materials, in particular the porosity, determines their properties. But in the mentioned works this impact is shown in different ways. For example, in the [3] the thermal conductivity of Fe (58.19 W/(m·K)) and of clay (3.26 W/(m·K)) differ by 18, but the thermal conductivity of insulation structures, which are made from granules of Fe and granules of clay with the same porosity are almost equal – 0.0403 W/(m·K) and 0.0402 W/(m·K).

Such results show that not only porosity, but also size and shape of the pores affect the properties of the material.

Since any material has an own characteristic distribution of the pore size, it is obvious that various researchers obtained conflicting information about the nature of the influence of pore size on the thermal properties of these materials. Current technologies of structure formation do not provide the prediction of the geometric structure, which means that there is no possibility to predict the properties of materials.

2. Literary analysis and the problem statement

In [1–4] the dependence of the thermal properties of porous materials on a structure was discussed, but recommendations about optimal structure were not given. In [5–7] the dependence of the mechanical properties on a structure of porous materials was analyzed and recommendations about structure formation with predicted properties were given, but there was no information about the thermal properties.

In [8] the influence of internal pore pressure on closed-cell elastomeric foams was explored. Changes of internal pore pressure with different hydrostatic loads were considered. Obtained results show that this pressure can significantly change macroscopic reaction and stability of closed-cell elastomeric foams. Also it shows that elastomeric foams with internal pore pressure have a higher stiffness, even with atmospheric pressure, than without it. But the method of calculating the internal pore pressure was not given. Also pressure was taken only as a function of density.

In [9] changes of the structure with a closed porosity under compression and extension, with different initial pressures in the pores, were researched. Experiment results show, that internal pressure has a positive effect under compression and negative under extension. The impact of deformation on the structures with closed porosity can lead to high initial pressure in the pores, which increases the total energy absorption and stiffness of the material under the process of deformation. But nothing was said about the methods of achieving certain pressure in the pores of the material and its calculation.

In [10] the micromechanical analysis of the porous material with internal pressure in the pores was made, the polymer BX-265 was taken as experimental material. The influence of initial pore pressure on the predicted elongation of the sample and the influence of the applied load (with pressure in the pores and without it) on the predicted break of the sample were shown. But nothing was said about the calculation methods of internal pore pressure.

In [11] the dependencies of thermal characteristics from the structure of materials were compiled and the task of the controlled pore formation by adjustable heat treatment of the raw gel-like mixture was formulated.

In [12–14] the main physicochemical formation processes of the gas-vapor area (pores) were analyzed, which were taken as a basis in this work.

All mentioned works have one main idea that materials structure affects their properties. But there are no practical recommendations about formation of specific material structure. Above information cannot be generalized, because it’s contradictory. That’s why existing technologies of the thermal swelling (structure formation) can’t give the required structure.

3. The purpose and objectives of the research

The purpose of this work is the research of regularities of gas-vapor phase formation in liquid mixtures, which are in a state of thermodynamic equilibrium.

To achieve this purpose, next objectives must be solved:

– to simulate the condition of thermodynamic phase equilibrium in the liquid mixture to control the process of pore formation;

– to determine the energy parameters of the swelling process (the pressure of the pore former agent gas inside the closed spherical pore, the conditions of thermal balance);

– to determine the overheating temperature of the liquid mixture to assess the growth dynamics of the gas-vapor area;

– to research the growth dynamics of the gas-vapor phase (pores).

4. Materials and methods of research

In this work, production technologies of porous heat–insulating materials were researched by the method of thermal swelling of the gel-like raw material mixture. When it is heated, inside the raw mass, are formed gas-vapor bubbles are formed, which after crystallization of the mixture form a porous space. Thermal conductivity of the material will depend from the size and shape of the resulting pores.

To obtain material as the active silica material, tuff, rotten stone, silicate – lump were used. The chemical composition of the materials is given in Table 1.

Table 1

The chemical composition of active silica materials

Name of material	Chemical composition, %				
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Tuff	93	2.8	0.5	0.6	0.1
Rotten stone	83	5.8	4.5	1.4	0.8
Silicate – lump	70	1.4	1.0	0.6	0.5

To obtain the raw mixture, quartz sand with SiO_2 – 97.7 % was used. The calculation of the amount of sodium hydroxide in the raw mixture is done in terms of Na_2O. Clay DN-1 has the following chemical composition, pts. wt.: Al_2O_3 – 33; Fe_2O_3 – 1.17. Refractoriness is 1690°C.

The ratio of the raw mixture components for the porous material production is shown in Table 2.

Table 2

The ratio of the raw mixture components

Component	pts. wt.
Siliceous rock	100
Mineral filler	1–75
Clay	1–75
Sodium hydroxide	1–15
Sodium bicarbonate	1–8
Water	50–125

Active silica material, mineral filler and clay were ground to the next specific surface areas: silica material – 1000 cm/g, filler – 4000 cm/g, clay – 1000 cm/g. Then ground components, sodium hydroxide and sodium bicarbonate (with appropriate concentrations) were mixed according to the ratio. The resulting mixture was steamed and then granulated to a grains size ≈20 mm. The granules were dried with air for 10–15 minutes at a temperature of 100–120 °C and then were swelled with heat treatment in a drying drum at a temperature of 500–550 °C for 5–20 minutes.

The obtained material has a low thermal conductivity even at temperatures of 1000–1200 °C (Fig. 1). The thermal conductivity of the material was determined by thermal conductivity meter IT – λ – 400. Samples with a cylindrical form (height 5 mm, diameter 15 mm) were put inside the meter and were processed by temperature influence from 200 to 700 °C. In this temperature range, the thermal conductivity of the material was determined according to the standard method, which is described in the device manual.

Fig. 1 shows the experimental dependence of thermal conductivity on the temperature of the material, for technologies of which the main technological stages were simulated.

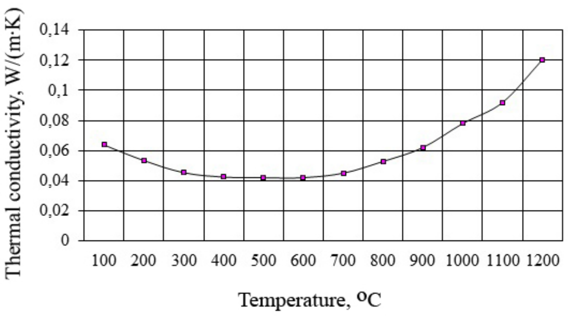


Fig. 1. Dependence of thermal conductivity on the temperature

5. Results of the research of regularities of phase transitions in liquid mixtures during heat treatment

5. 1 Equilibrium conditions of the pore agent in the material, during the formation of the porous structure

As the dynamic characteristic, which determines the direction of size changes in vapor pore, tension difference was taken, which was caused by the pressure in the vapor area and by the resistance of the boundary surface of the pore.

The equation, which characterizes the dynamics of growth or reduction of the vapor bubble [11]

$$\frac{dw}{d\tau}=-\frac{1{,}5\rho w^2+P_g-P_p(T)}{\rho_g R}=-\frac{1{,}5\rho w^2}{\rho_g R}+\frac{P_p(T)-P_g}{\rho_g R}, \quad (1)$$

where w – speed of growth of the vapor bubble; τ – time of bubble growth; ρ – density; P_p – pressure inside the vapor area; P_g – pressure in the surrounding liquid; T – temperature; R – radius of the vapor bubble.

Increasing, decreasing and stabilization of the bubble sizes can be represented by three cases:

$$\begin{cases} \dfrac{P_p(T)-P_g}{1{,}5\rho}>0, & \dfrac{\sqrt{1{,}5\rho}}{2\sqrt{P_p(T)-P}}\ln\left|\dfrac{w-\sqrt{\dfrac{P_p(T)-P_g}{1{,}5\rho}}}{w+\sqrt{\dfrac{P_p(T)-P_g}{1{,}5\rho}}}\right|=-\dfrac{1{,}5\rho\tau}{\rho_g R}+C; \\ \dfrac{P_p(T)-P_g}{1{,}5\rho}<0, & \sqrt{\left|\dfrac{1{,}5\rho}{P_p(T)-P_g}\right|}\operatorname{arctg}\sqrt{\left|\dfrac{1{,}5\rho}{P_p(T)-P_g}\right|}w=-\dfrac{1{,}5\rho\tau}{\rho_g R}+C; \quad (2) \\ \dfrac{P_p(T)-P_g}{1{,}5\rho}=0, & \dfrac{1}{w}=-\dfrac{1{,}5\rho\tau}{\rho_g R}+C. \end{cases}$$

When $P_p(T)-P>0$ – vapor bubble is increasing, $P_p(T)-P<0$ – vapor bubble is decreasing, in case when $P_p(T)-P=0$ – size of the vapor bubble is stabilized. As can be seen from the equations, $P_p(T)$ depends on the external heat flow (temperature). Therefore, the process of pore formation can be controlled.

Speed of size changing of the vapor bubble can be found by the next equations

$$w(\tau)=\begin{cases} \sqrt{\dfrac{P_p(T)-P_g}{1{,}5\rho}}\dfrac{1+k(\tau)}{1-k(\tau)};\ \dfrac{P_p(T)-P_g}{1{,}5\rho}>0, \\ \sqrt{\left|\dfrac{P_p(T)-P_g}{1{,}5\rho}\right|}\operatorname{tg}\sqrt{\left|\dfrac{P_p(T)-P_g}{1{,}5\rho}\right|}\left(C-\dfrac{1{,}5\rho\tau}{\rho_g R}\right);\dfrac{P_p(T)-P_g}{1{,}5\rho}<0, \quad (3) \\ \dfrac{\rho_g R}{1{,}5\rho\tau-C\rho_g R};\ P_p(T)-P=0. \end{cases}$$

With

$$\frac{(w-\alpha)(w_0+\alpha)}{(w+\alpha)(w_0-\alpha)}=e^{-\frac{1{,}5\rho\tau}{\rho_g R}},$$

final equations will be the next

$$\begin{cases} w=\dfrac{\alpha\left[(w_0-\alpha)e^{-\frac{1{,}5\rho\tau}{\rho_g R}}+w_0+\alpha\right]}{w_0+\alpha-(w_0-\alpha)e^{-\frac{1{,}5\rho\tau}{\rho_g R}}};\ \alpha=\sqrt{\dfrac{P_p(T)-P_g}{1{,}5\rho}};\dfrac{P_p(T)-P_g}{1{,}5\rho}>0, \\ w=\dfrac{\sqrt{\left|\dfrac{1{,}5\rho}{P_p(T)-P_g}\right|}w_0-\operatorname{tg}\dfrac{1{,}5\rho\tau}{\rho_g R}}{\sqrt{\left|\dfrac{1{,}5\rho}{P_p(T)-P_g}\right|}+\left|\dfrac{1{,}5\rho}{P_p(T)-P_g}\right|w_0\operatorname{tg}\dfrac{1{,}5\rho\tau}{\rho_g R}};\quad \dfrac{P_p(T)-P_g}{1{,}5\rho}<0, \quad (4) \\ w=\dfrac{w_0\rho_g R}{1{,}5\rho w_0\tau-\rho_g R};\ P_p(T)-P_g=0. \end{cases}$$

In the last case, when $P_p(T)-P_g=0,$ the gas-vapor area (pore) doesn't change in volume. In the technological aspect, relations between energetic parameters, which characterize the predicted pore size (average), were achieved. Therefore, thermophysical parameters also were achieved, including thermal conductivity. If $w_0\neq 0,$ the latter equation loses the physical sense, because for this case $w=0.$

The equation for finding the speed of size changing of the pore, can be written as

$$\frac{dR}{d\tau}=\frac{w_0\rho_g R}{1{,}5\rho w_0\tau-\rho_g R}. \quad (5)$$

When solving the equation (5), duration of the swelling process can be found. Since the average value of the pore size is one of the main factors, which determine thermophysical properties of the sample, it this method gives a chance to predict the discussed properties. For example, the thermal conductivity of the material from section 4.

This method allows assessing the kinetic parameters of thermal swelling with sufficient accuracy. For chemical pore formation, the method should be supplemented by the energy estimate of the probability of such reaction, which can be assessed by the Gibbs energy equation.

The Gibbs energy of the pores embryo with radius r (under thermal or chemical swelling)

$$G^{(1)}=\varphi_\infty^{(1)}M^{(1)}+\sigma\Omega, \quad (6)$$

where $M^{(1)}$ – mass of the pore former, which equals $4\pi r^3/\upsilon'$; Ω – outside surface of the pore former, which equals $4\pi r^2$; $\varphi_\infty^{(1)}$ – chemical potential of the pore former gas (with infinitely large volume of this gas).

The Gibbs energy of the system, which consists of the pores embryo in the material

$$G = G^{(1)} + G^{(2)},$$

where $G^{(2)}$ – the Gibbs energy of the material.

Let's consider the equilibrium state of the system. If the external pressure p′ equal to the pore former pressure and temperature of the system T′ are constant, the equilibrium condition dG=0 will be the next

$$\begin{aligned} &dU^{(1)} + dU^{(2)} - T'\left(dS^{(1)} + dS^{(2)}\right) + \\ &+p'\left(dV^{(1)} + dV^{(2)}\right) + \varphi_\infty^{(1)} dM^{(1)} + \varphi^{(2)} dM^{(2)} = 0. \end{aligned} \tag{7}$$

Considering that

$$\left(\frac{\partial U}{\partial S}\right)_V = T; \ \left(\frac{\partial U}{\partial V}\right) = -p,$$

for gas bubble according to the Laplace's equation [15]

$$-p^{(1)} = -\left(-p' - \frac{2\sigma}{r}\right),$$

find

$$\begin{aligned} &dU^{(1)} + dU^{(2)} = T^{(1)} dS^{(1)} + \\ &+T^{(2)} dS^{(2)} - \left(p' - \frac{2\sigma}{r}\right) dV^{(1)} - p' dV^{(2)}, \end{aligned}$$

where p – external pressure (in this case, pressure of the material on the pore former agent).

Considering that the total mass of the system is constant

$$dM^{(2)} = -dM^{(1)},$$

from the equilibrium condition

$$\frac{2\sigma}{r} dV^{(1)} + \left(\varphi_\infty^{(1)} - \varphi^{(2)}\right) dM^{(1)} = 0.$$

For spherical pore former agent

$$V^{(1)} = 4\pi r^2 dr;$$

$$dM^{(1)} = \frac{4\pi r^2}{\upsilon^{(1)}} dr.$$

That's why, the latter ratio can be written as

$$\left(\varphi_\infty^{(1)} - \varphi^{(2)} + \frac{2\sigma\upsilon^{(1)}}{r}\right) dr = 0,$$

or, as dr≠0,

$$\varphi^{(2)} - \varphi_\infty^{(1)} = \frac{2\sigma\upsilon^{(1)}}{r}. \tag{8}$$

If instead $\varphi_\infty^{(1)}$ and $\varphi^{(2)}$, take real values of the chemical potentials of the pore former agent and material, with the temperature and corresponding pressure, $\varphi^{(1)}\left(p^{(1)}, T\right)$ and $\varphi^{(2)}\left(p^{(2)}, T\right)$ will be obtained. Using analogy with the gas bubble in an infinite liquid volume (expansion of $\varphi^{(1)}\left(p^{(1)}, T\right)$ in a series in $p^{(1)} - p^{(2)}$, and of $\varphi^{(2)}\left(p^{(2)}, T\right)$ in a series in $p^{(2)} - p^{(1)}$ [15]) $\varphi^{(1)}\left(p^{(1)}, T\right) = \varphi^{(2)}\left(p^{(2)}, T\right)$ can be found.

From the resulting equation it follows that if boundary surface is not flat, chemical potentials of the pore former agent and material related to its own pressure and total temperature are equal. Therefore, equilibrium conditions of the pore former agent in the material under formation of the porous structure with surface tension can be written as

$$\begin{cases} T^{(1)} = T^{(2)}; \\ p^{(1)} - p^{(2)} = \dfrac{2\sigma}{r}; \\ \varphi^{(1)}\left(p^{(1)}, T\right) = \varphi^{(2)}\left(p^{(2)}, T\right). \end{cases} \tag{9}$$

5. 2. Pressure of the pore former agent gas inside a closed spherical pore

After differentiating the equation (8) by pressure p, with T=const and $\left(\partial\varphi / \partial p\right)_T = \upsilon$, the next equation will be obtained

$$\frac{1}{\rho^{(2)}} - \upsilon^{(1)} = -\frac{2\upsilon^{(1)}\sigma}{r^2}\left(\frac{\partial r}{\partial p}\right)_T + \frac{2\sigma}{r}\left(\frac{\partial \upsilon^{(1)}}{\partial p}\right)_T. \tag{10}$$

As $\frac{1}{\rho^{(2)}}$ is much smaller than $\upsilon^{(1)}$, and $\upsilon^{(1)}$ at relatively low gas pressures can be equal to RT/p, then

$$\frac{RT}{p^{(1)}} = \frac{2\upsilon^{(1)}\sigma}{r^2}\left(\frac{\partial r}{\partial p}\right)_T - \frac{2\sigma}{r}\left(\frac{\partial \upsilon^{(1)}}{\partial p}\right)_T.$$

After integrating this equation by p≥0

$$\int \frac{RT}{p^{(1)}} dp = \int \frac{2\upsilon^{(1)}\sigma}{r^2}\left(\frac{\partial r}{\partial p}\right)_T dp - \int \frac{2\sigma}{r}\left(\frac{\partial \upsilon^{(1)}}{\partial p}\right)_T dp,$$

$$RT \cdot \left[\ln\left(p^{(1)} + c\right)\right] = -2\sigma\frac{\upsilon^{(1)}}{r},$$

where c – integration constant.

After transformations

$$p^{(1)} = e^{-c} \cdot e^{-\frac{2\sigma}{RT}\frac{\upsilon^{(1)}}{r}}.$$

The constant e^{-c} is found from equilibrium conditions, provided that when $r \to \infty$, $p = p_0$, i. e. the pressure of the pore former agent equals to pressure of gas under the same physical conditions, outside of the material

$$p^{(1)} = p_0 \cdot e^{-\frac{2\sigma}{RT}\frac{\upsilon^{(1)}}{r}}. \tag{11}$$

From this equation it follows that in equilibrium the pressure of the gas pore former gas inside the pore is smaller than the pressure of this gas outside of the material by $e^{\frac{2\sigma}{RT}\frac{\upsilon^{(1)}}{r}}$ times.

Obtained equation also can be written as

$$p^{(1)} = p_0 \cdot e^{-\frac{E_a}{RT}}, \tag{12}$$

where $E_a = 2\sigma^{\frac{\upsilon^{(1)}}{r}}$ or like in (1), $E_a = \varphi^{(2)} - \varphi_{\infty}^{(1)}$ – activation energy, which equals to the difference between the chemical potentials of the material and the pore former agent.

Equation (6) shows that the larger the difference between the chemical potentials of material-pore systems, the lower the pressure of gas inside the pores. Since the convective heat transfer in a gas is directly proportional to the pressure, next statement can be made: to achieve minimum heat transfer of the pore, it's necessary to increase the difference between the chemical potentials of material-pore systems.

5. 3. Temperature of the pore former agent gas inside a closed spherical pore

From [14] it's known that the temperature of the phase transition of the spherical drop in vapor is higher than the temperature of the phase transition from the surface. This means that it is necessary to overheat the liquid inside the pores, so that it turned into vapor, at the temperature

$$\Delta T = \frac{2\sigma\upsilon'' T}{Lr}, \tag{13}$$

where υ'' – volume of saturated vapor; L – heat of vaporization; σ – coefficient of surface tension at the temperature T_S (i. e. before the curvature of the surface was changed).

Equation (13) applies to vapor bubble, which is in equilibrium with the environment. It can be used to determine the degree of liquid overheat, which does not contain dissolved gases and which is boiling under constant external pressure on the liquid.

The temperature of the pore former gas, which is in equilibrium, can be found by the temperature of the material. After differentiating the equation (9) by T, with $(\partial\phi/\partial T)_P = -s$ and $(\partial\varphi/\partial p)_T = \upsilon$, the equation will be

$$\left(\frac{\partial\phi^{(1)}}{\partial p}\right)_T \frac{dp}{dT} + \left(\frac{\partial\phi^{(1)}}{\partial T}\right)_P = \left(\frac{\partial\phi^{(2)}}{\partial p}\right)_T \frac{dp}{dT} + \left(\frac{\partial\phi^{(2)}}{\partial T}\right)_P;$$

$$\frac{dp}{dT} = \frac{s^{(2)} - s^{(1)}}{v^{(2)} - v^{(1)}}.$$

or

$$dT = \frac{1}{s^{(2)} - s^{(1)}}\left(\frac{1}{\rho^{(2)}} \cdot dp^{(2)} - v^{(1)} \cdot dp^{(1)}\right).$$

Since the density of the material is almost independent of the pressure, at low gas pressures $v = RT/p$, so

$$T = \frac{1}{s^{(2)} - s^{(1)}}\left(\frac{p^{(2)}}{\rho^{(2)}} - RT\ln\left|p^{(1)}\right|\right) + \text{const}. \tag{14}$$

After differentiating the equation (7) by temperature T, with $(\partial\phi/\partial T)_P = -s$ and P=const, the equation will be

$$s^{(1)} - s^{(2)} = -\frac{2\sigma v^{(1)}}{r^2}\left(\frac{\partial r}{\partial T}\right)_P + \frac{2\sigma}{r}\left(\frac{\partial v^{(1)}}{\partial T}\right)_P.$$

At equilibrium conditions, the embryo radius of the pore former and its volume do not depend on the temperature, so if pressure is constant

$$s^{(2)} - s^{(1)} = -\frac{2\sigma v}{rT}.$$

With the equation (14) (when $r \to \infty$), the overheat temperature of the pore former agent gas inside the pore will be

$$\Delta T = \frac{1}{R\ln\left|p^{(1)}\right|} \cdot \left(\frac{2\sigma v^{(1)}}{r} + \frac{p^{(2)}}{\rho^{(2)}}\right) - T_0, \tag{15}$$

where T_0 – temperature of the pore former gas under the same physical conditions outside the pore.

5. 4. Heat transfer between the growing pore and the surrounding mixture

The equation of heat balance for a single vapor bubble

$$(T_0 - T_s) \cdot \lambda_1 \cdot \left(\frac{2}{\delta} + \frac{1}{r}\right) = -j(T_s) \cdot L(T_s) - q(T_s), \tag{16}$$

where δ – current thickness of the thermal boundary layer; j – density of the material flux; L – heat of condensation; λ_1– coefficient of thermal conductivity of the liquid; q – heat flux density.

The equation for the pore inside the flux of mixture, will be

$$\Delta T \cdot \lambda_1 \cdot \left(\frac{2}{\delta} + \frac{1}{r}\right) = -p_0 \cdot e^{-\frac{Ea}{RT}} \cdot \left.\frac{dr}{d\tau}\right|_{\tau=0}^{\tau=\tau'} - q_{P=\text{const}}, \tag{17}$$

where $q_{P=\text{const}}$ – heat flux density in the isobaric stage; τ' – time of the first stage of pore growth.

In the main stage of pore growth (isobaric) heat, which is supplied to the growing pore from the surrounding mixture, will be

$$Nu \sim Re^n \cdot Pr^m. \tag{18}$$

The average in time, pore radius will be

$$\bar{r} = \frac{1}{\tau - \tau'} \int_{\tau=\tau'}^{\tau} r(\tau)d\tau, \tag{19}$$

and with the dependence of time from pore radius in the isobaric stage of pore growth

$$\bar{r} = \frac{\sqrt{6}}{1{,}83} \cdot \frac{\tau^2}{\tau - \tau'} \cdot \sqrt{\frac{p - p_0}{\rho}}. \tag{20}$$

The Nusselt number

$$Nu = \frac{q_{P=\text{const}} \cdot \bar{r}}{\lambda \cdot \Delta T}. \tag{21}$$

The Reynolds number

$$Re = \frac{\bar{r}}{\nu} \cdot \frac{dr}{d\tau}. \tag{22}$$

If substitute these equations in the heat transfer equation, we will get

$$\frac{q_{P=\text{const}}}{\lambda \cdot \Delta T} = \text{const} \cdot \frac{(\bar{r})^{n-1}}{\nu^n}\left(\frac{dr}{d\tau}\right)^n \cdot Pr^m. \tag{23}$$

With average pore radius, will be

$$q_{P=\mathrm{const}} = \mathrm{const} \cdot \Delta T \times$$
$$\times \frac{\left(\frac{\tau^2}{\tau - \tau'} \cdot \sqrt{\frac{p - p_0}{\rho}} \right)^{n-1}}{\nu^n} \left(\frac{dr}{d\tau} \right)^n \cdot \frac{(\mu \cdot c_p)^m}{\lambda^{m-1}}. \tag{24}$$

Final heat balance equation of growing pore in the initial mixture with isothermal stage

$$\Delta T \cdot \lambda_1 \cdot \left(\frac{2}{\delta} + \frac{1}{r} \right) = -p_0 \cdot e^{-\frac{Ea}{RT}} \times$$
$$\times \frac{dr}{d\tau}\bigg|_{\tau=0}^{\tau=\tau'} - \mathrm{const} \cdot \Delta T \cdot \frac{(\mu \cdot c_p)^m}{\lambda^{m-1}} \cdot \frac{\left(\frac{\tau^2}{\tau - \tau'} \cdot \sqrt{\frac{p - p_0}{\rho}} \right)^{n-1}}{\nu^n} \left(\frac{dr}{d\tau} \right)^n \bigg|_{\tau=\tau'}^{\tau}. \tag{25}$$

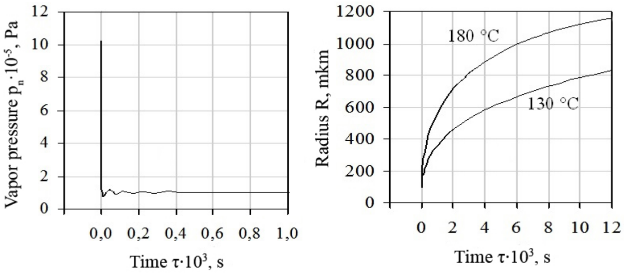
This equation will be used in the description of the growth process and stabilization of the gas-vapor area in the liquid raw mixture, under heat treatment and swelling. With the equation (25) the quantity of energy, required for the realization of the above process, can be found.

6. The analysis of the received results of calculation of the gas-vapor area of the pore

Calculation of the gas-vapor area (pore) will be made with using the equation (25). The calculation purpose is the prediction of growth dynamics of the pores. As dependences of pore size from time (5) with different levels of energy influence on the mixture (11), (15), (16) are known, the process of heat treatment and final pores size can be controlled. It means that thermophysical properties of the material can be predicted.

Calculations were made by the finite difference method (Fig. 2, 3).

The raw mixture (Table 2) was swollen under temperatures 110–190 °C. Temperatures were found by differential thermal analysis. In this temperature range the first exothermic effect, associated with evaporation of the moisture, was observed.



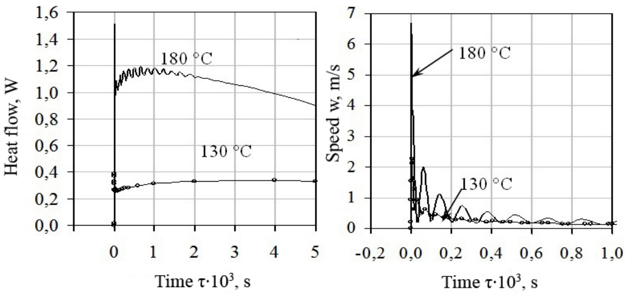
a *b*

Fig. 2. Changing in the time of: *a* — vapor pressure; *b* — pore radius under swelling temperatures 130 °C and 180 °C

Decreasing of the heat flow under increasing radius can be seen in Fig. 3, *a*. This happened because of reduction of the temperature difference between a raw mix and vapor. The radius changes in time (Fig. 2, *b*), but characteristic oscillations of the radius are not observed, because the mass flow is able to compensate the expansion effect of the vapor volume (reducing of the vapor density). The curves of movement speed changes of the water-vapor boundary (Fig. 3, *b*) are similar in the character of changing in time. The initial jump of the mass flow and movement speed of the water-vapor boundary, are the result of the sharp decline of the temperature and vapor density, which also led to decreasing of vapor pressure (Fig. 2, *a*).

The oscillations of vapor pressure (Fig. 1, *a*) are the result of the combined effect of temperature and vapor density. And if $p_p = f(T_p)$ is used in calculations, results will be incorrect. Vapor pressure has an oscillatory character of changing in time with constantly decaying amplitude, which leads to some balance of vapor pressure.

The results of calculations for initial temperature t_0=130 °C can be seen in Fig. 2, 3. Reducing the temperature to this value leads to a reduction of the oscillations of measured quantities, or to complete disappearance of them.



a *b*

Fig. 3. Changing in the time of: *a* — heat flow to vapor; *b* — movement speed of the pore boundary under swelling temperatures 130 °C and 180 °C

The character of movement speed changes of the water-vapor boundary (Fig. 3, *b*) is consistent with the change of vapor temperature T_p, as with temperature 180 °C. In general, the peak values of the growth speed of vapor volume (Fig. 3, *a*), movement of the pore boundary, mass flow, heat flow have smaller values under lower periods of oscillations. The general character of changing of the calculated values under 130 °C and 180 °C is the same.

The character of changing of the measured quantities for the vapor pore radius 10 and 500 mkm is the same, as with 100 mkm, but amplitude quantities increase with decreasing radius. At a small value R, the curve changing shows a sharp decrease of the mass flow, which is caused by a decrease of heat gain from the water, as a result of its intensive cooling (rapid decline of temperature T). Increasing of the mass flow with R_3=500 mkm is caused by the longer heat gain from the water.

Equations of the growth model of vapor phase were used for calculation of the distribution of pressure near the growing vapor value area, for certain radiuses. Results of calculation can be seen in Fig. 4.

Experimental and calculation results of pressure distribution in time have good coherence in the frequency of pressure change. The mismatch of the pressure change amplitude is due to the fact that in the calculation the drop with spherical shape was taken, but the real drop hasn't ideal spherical shape.

In the calculation, the period of vapor phase formation until the size 1 mkm wasn't considered. This assumption is taken into account by the equation (15). But Fig. 4 shows that appearance of each individual bubble can be identified with the formation of a vapor layer with a certain size. Comparison of the experimental and calculated data shows the relative error in the determination of the pulse pressure ≈15.8 %.

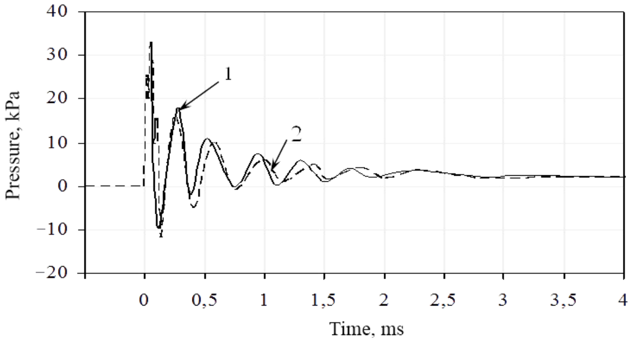


Fig. 4. Comparison of calculated (curve 1) and experimental (curve 2) data of growth of the vapor phase under boiling water

Verification of equations, based on indirect estimates (pressure, temperature) and comparison of the calculated pore size with real allows making a conclusion about the adequacy of the proposed methodology of assessing the main parameters of the swelling process.

The main advantages of the proposed method are the ability to assess the energy impact on the liquid raw mixture, determine the conditions of controlled swelling and controlled structure formation of the material with the predicted thermal properties. These results are proposed to use in designing technological processes of production of porous materials for various purposes.

The continuation of this work will be the study of physical and chemical phenomena in the material during its heat treatment, to optimize the composition of the raw liquid mixture.

7. Conclusions

1. Equilibrium conditions of the pore former agent in the material during the formation of the porous structure, with account of surface tension

$$\begin{cases} T^{(1)} = T^{(2)}; \\ p^{(1)} - p^{(2)} = \dfrac{2\sigma}{r}; \\ \varphi^{(1)}\left(p^{(1)}, T\right) = \varphi^{(2)}\left(p^{(2)}, T\right). \end{cases}$$

These conditions allow estimating the energy parameters of the swelling process.

2. Pressure of the pore former agent gas inside the closed spherical pore in equilibrium state

$$p^{(1)} = p_0 \cdot e^{-\frac{E_a}{RT}},$$

where $E_a = \varphi^{(2)} - \varphi_{\infty}^{(1)}$ – activation energy, equal to the difference between the chemical potentials of the material and pore former agent.

The bigger the difference between the chemical potentials of material-pore systems, the lower the gas pressure will be inside the pore. Since the convective heat transfer in a gas is directly proportional to the pressure, next statement can be made: to achieve minimum heat transfer of the pore, it's necessary to increase the difference between the chemical potentials of material-pore systems.

3. Overheat temperature of the pore former agent gas inside the closed spherical pore in equilibrium state

$$\Delta T = \frac{1}{R \ln\left|p^{(1)}\right|} \cdot \left(\frac{2\sigma v^{(1)}}{r} + \frac{p^{(2)}}{\rho^{(2)}} \right) - T_0,$$

where T_0 – temperature of the pore former gas under the same physical conditions outside the pore.

This equation was used for assessing the intensity of the material structure formation.

4. The gas-vapor area was calculated. Obtained equations give a chance to calculate size changing of the pore in time with different levels of energy influence on the mixture and give a chance to control structure formation of the material with predicted properties.

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