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DIMENSIONS OF THE NUCLEUS AGENT PORE FORMER CLOSED SPHERICAL PORES

Introduction

Many experimental data indicate a relationship between the porosity of the material and its thermophysical properties [1-3]. Influence of porosity on the thermal conductivity of the material can be considered following the example of experimental data [2]. The values of thermal conductivity coefficient of iron (58.19 W/(m·K)) and a rock formation (3.26 W/(m·K)) differ by almost 18 times, but the filling of iron balls and balls rock formation of the same a porosity of 62.5% has nearly the same coefficient of thermal conductivity (0.0403 W/(m·K) and 0.0402 W/(m·K) respectively). However, the way of forming the porous structure has not yet been investigated, and a clear relationship between the porosity and the physical properties of the material not found.

Purpose and objectives of the research

The purpose is to find the critical diameter of the nucleus pores.

To achieve this purpose following objectives were set:

- Finding the equilibrium conditions of gas blowing agent in the porous material.
- Determination of the gas pressure a blowing agent inside the closed pores is spherical in an equilibrium state.
- Finding the critical diameter of the nucleus a blowing agent.

Analysis of the literature data on the change of pressure in the pores

In [4] conducted research on the effect of pore pressure on elastomers with closed porosity. The change in the pore pressure at different hydrostatic loads and shown that this pressure can significantly alter the macroscopic reaction and stability of elastomers with closed porosity. It was also shown that porous elastomers have higher rigidity when there is pressure in the pores, even atmospheric than in its absence. However, during the study to provide a method for calculating the pore pressure and the initial pressure was taken the ambient pressure. It is also assumed that the pressure in the pores is a function of density.

In [5] studied the variation structure with closed porosity under compression and extension at different initial pressures in the pores. The experimental results showed that the pressure in the pores positively affects during compression and tensile negatively. Impact deformation on the structure with a closed porosity can lead to high internal pressure in the pores, which leads to an increase in the absorption of energy and the overall stiffness of the material during the deformation. But it was not reviewed by methods to achieve those or other pressure in the pores of the material and the method of their calculation.

The equilibrium conditions blowing agent in the material during the formation of the porous structure

The Gibbs energy of the nucleus pore radius r

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

where: $M^{(1)}$ – the mass of blowing agent, which is equal to $4\pi r^3/\nu'$; Ω – the outer surface of the blowing agent, is equal to $4\pi r^2$; $\varphi_{\infty}^{(1)}$ – the chemical potential of the foaming gas (for an infinitely large volume of gas).

The Gibbs energy the system consisting of the nucleus pores in the material

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

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

Consider the state of equilibrium of the system. If the external pressure p' , coinciding with the blowing agent pressure and temperature T' , where there is a system constant, the equilibrium condition $dG = 0$ has the form

$$dU^{(1)} + dU^{(2)} - T'(dS^{(1)} + dS^{(2)}) + p'(dV^{(1)} + dV^{(2)}) + \varphi_{\infty}^{(1)} dM^{(1)} + \varphi^{(2)} dM^{(2)} = 0$$

Is meant that

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

for the gas bubble according to the formula of Laplace [6]

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

we find

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

where p' is an external pressure (in this case, the pressure of the material to an blowing agent).

Taking into account that, due to the constancy of the total mass of the system

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

from the equilibrium condition we obtain

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

For a spherical blowing agent

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

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

Therefore, the last relation can be written as

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

or an because $dr \neq 0$

$$\varphi^{(2)} - \varphi_{\infty}^{(1)} = \frac{2\sigma\nu^{(1)}}{r} \quad (1)$$

Consider instead $\varphi_{\infty}^{(1)}$ and $\varphi^{(2)}$ the actual values of the chemical potentials blowing agent and of the material at a given temperature and corresponding pressure of $\varphi^{(1)}(p^{(1)}, T)$ and $\varphi^{(2)}(p^{(2)}, T)$. By analogy with the gas bubbles in the infinite volume of fluid (expanding $\varphi^{(1)}(p^{(1)}, T)$ a series in powers $p^{(1)} - p^{(2)}$, $\varphi^{(2)}(p^{(2)}, T)$ a series in powers $p^{(2)} - p^{(1)}$ [7]) can be obtained

$$\varphi^{(1)}(p^{(1)}, T) = \varphi^{(2)}(p^{(2)}, T)$$

From the obtained equation it follows that if different from the plane of the interface chemical potential blowing agent and material, referred to the self-pressure and total temperature are of equal importance. Thus, the equilibrium conditions of the blowing agent in the material during the formation of the porous structure, taking into account surface tension, are of the form

$$\left\{ \begin{array}{l} T^{(1)} = T^{(2)} \\ p^{(1)} - p^{(2)} = \frac{2\sigma}{r} \\ \varphi^{(1)}(p^{(1)}, T) = \varphi^{(2)}(p^{(2)}, T) \end{array} \right. \quad (2)$$

The gas pressure blowing agent inside the closed spherical pores

Differentiating equation (1) on pressure p at $T = \text{const}$ and considering that $(\partial\varphi/\partial p)_T = \nu$, we obtain

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

Because $\frac{1}{\rho^{(2)}}$ much less than $\nu^{(1)}$, a $\nu^{(1)}$ at relatively low gas pressures can be assumed equal RT/p then

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

Integrating this equation $p \geq 0$ we obtain

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

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

where c is integration constant.

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

The constant e^{-c} we find from the condition of equilibrium, given that the $r \rightarrow \infty$, $p = p_0$ i.e. pressure agent, blowing agent is equal to the pressure of the gas under the same physical conditions outside material

$$p^{(1)} = p_0 \cdot e^{\frac{2\sigma v^{(1)}}{RT r}} \quad (3)$$

From this equation it follows that the a state of equilibrium pressure of the gas blowing agent within the pores smaller pressure of this gas in the of the outside material in $e^{\frac{2\sigma v^{(1)}}{RT r}}$ times.

This equation can also be written in the form

$$p^{(1)} = p_0 \cdot e^{-\frac{E_a}{RT}} \quad (4)$$

where $E_a = 2\sigma \frac{v^{(1)}}{r}$ or according to (1) $E_a = \varphi^{(2)} - \varphi_{\infty}^{(1)}$ - activation energy, equal to the difference between the chemical potentials of the material and the blowing agent.

From equation (4) it follows that the greater the difference in chemical potential material systems pore, the lower the pressure will be in the gas inside the pores. Because convective heat transfer in a gas is directly proportional to depend on the pressure, then this statement can be paraphrased as follows: to achieve the minimum heat transfer necessary to increase the pores difference between the chemical potentials of the system, material-pores.

Dimensions of the nucleus agent pore former closed spherical pores

If in the material of is formed a certain amount of blowing agent, the Gibbs energy of the entire system is changed to a value comprised of two members, the first of which is equal to the product of the difference between the chemical potentials of the new and the original gas on amount of generated the blowing agent. The second member of equation is due to the surface energy and equal to the surface tension on the surface area of pores.

$$\Delta G = (\varphi^{(1)} - \varphi^{(1pre)}) \Delta M^{(1)} + \sigma \Omega \quad (5)$$

For a spherical particle

$$\Delta M^{(1)} = \frac{4}{3} \cdot \frac{\pi}{v'} r^3; \quad \Omega = 4\pi r^2 \quad (6)$$

therefore

$$\Delta G = \frac{4\pi}{3} (\varphi^{(1)} - \varphi^{(1pre)}) \frac{r^3}{v^{(1)}} + 4\pi \sigma r^2 \quad (7)$$

Differentiating equation of the Gibbs energy changes of the radius of the equation and equate to zero

$$\left(\varphi_{\infty}^{(1)} - \varphi_{\infty}^{(1pre)} \right) \frac{\left(r_{cr}^{(1)} \right)^2}{v^{(1)}} + 2\sigma r_{cr}^{(1)} = 0$$

In this equation, the values of the chemical potentials of substances outside pores that would bring them a sign of differentiation.

The values of $r_{cr}^{(1)}$ will be equal to

$$r_{cr}^{(1)} = \frac{2\sigma\nu^{(1)}}{\varphi_{\infty}^{(1pre)} - \varphi_{\infty}^{(1)}} \quad (8)$$

where: $\varphi_{\infty}^{(1pre)}$ – the chemical potential of the source material blowing agent; $\varphi_{\infty}^{(1)}$ – chemical potential blowing agent outside pores.

If the original material is formed nucleus pore of radius $r_{cr}^{(1)}$ it will be in equilibrium with the surrounding material. The gas pressure blowing agent pores is less than the pressure of the same gas in the surrounding environment and smaller pressure exerted by the surrounding material (equation (4)). This means that the equilibrium state is metastable. Without supply to external energy the pore or reduce stress tensor nucleus pores will disappear – it will be absorbed by material.

When $r^{(1)} > r_{cr}^{(1)}$ there are several options for development.

The first possibility is, if $\varphi^{(1)} - \varphi^{(1pre)} < 0$ and r is small, the second member in the expression (7) will prevail. With a further decrease r , ΔG will increase, i.e. the formation of the nucleus of very small size pores will lead to an increase in energy Gibbs. Increasing ΔG it will continue as long as the first and second members in the expression for $\partial G / \partial r$ are not equal before r not reaches such a value $r = r_{cr}^{(1)}$, in which the Gibbs energy reaches a maximum, and at $r > r_{cr}^{(1)}$ decreasing. The above is shown schematically in Figure 1.

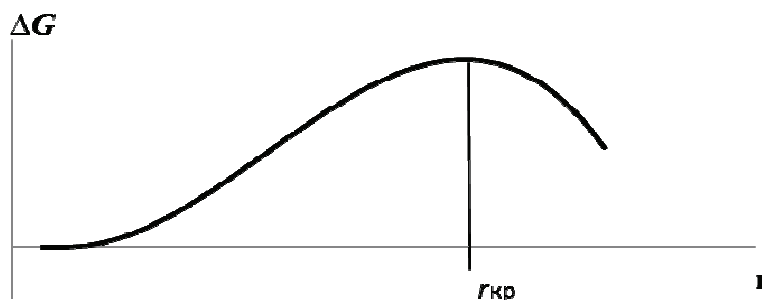


FIGURE 1. Changes in of the Gibbs energy of the radius at $\varphi^{(1)} - \varphi^{(1pre)} < 0$ and small r

The second possibility – when $\varphi^{(1)} - \varphi^{(1pre)} > 0$, if for any values r the Gibbs energy increases, and the system tends to absorb pores.

In any case, if the original size of arising of the nucleus less than $r_{cr}^{(1)}$, then the nucleus cannot exist for a long time and will rapidly decrease in size until complete disappearance.

For the existence of pores is necessary to $\varphi^{(1)} - \varphi^{(1pre)} < 0$ and $r > r_{cr}^{(1)}$. At the same time critical radius is directly proportional to the surface tension coefficient. Pores in the initial mixture is more likely to occur in areas with low surface tension (data field may be generated by fluctuations in density).

Features of formation of nuclei been discussed in the chapter – the genesis of vaporization.

The work of formation and time when occurrence the of the nucleus pores

The work of the reversible formation of a spherical nucleus of pores $l_{min}^{(1)}$ in conditions $T = \text{const}$, $V = \text{const}$

$$l_{min}^{(1)} = -\left(p^{(1)} - p\right) \frac{4}{3} \pi r^{(1)3} + 4\pi r^{(1)2} \sigma$$

Before the formation of the nucleus volume the initial phase was equal to $V+V^{(1)}$ (where $V^{(1)} = \frac{4}{3}\pi r^{(1)3}$), pressure p ; after the formation of the nucleus volume remains the same, and the pressure in the region of space where appeared an nucleus, was equal to $p^{(1)}$, decreased by $p-p^{(1)}$. Accordingly, was spent work $-\int V^{(1)}dp = -(p^{(1)}-p)\frac{4}{3}\pi r^{(1)3}$, moreover, in the expression $l_{\min}^{(1)}$ included surface energy $4\pi r^{(1)2}\sigma$.

Because

$$p^{(1)} - p = \frac{2\sigma}{r^{(1)}}$$

then the expression for $l_{\min}^{(1)}$ reduced to the form

$$l_{\min}^{(1)} = \frac{4}{3}\pi\sigma r^{(1)2} \tag{9}$$

As can be seen from the equation (9) work on the appearance of the nucleus and job growth of pores are different.

The work formation of the nucleus pores critical size will be equal to

$$l_{cr}^{(1)} = \frac{16}{3}\pi\sigma^2 \frac{\nu^{(1)}}{\varphi_{\infty}^{(1pre)} - \varphi_{\infty}^{(1)}}$$

or an given that $r^{(1)} = \frac{2\sigma}{p^{(1)} - p}$

$$l_{cr}^{(1)} = \frac{16}{3}\pi \frac{\sigma^3}{(p_{cr}^{(1)} - p)^2}$$

The frequency of spontaneous appearance of the nucleus can be represented as [7]

$$J = N_1 \cdot B \cdot e^{-\frac{l_{cr}^{(1)}}{k_B \cdot T}}$$

where: N_1 – amount of blowing agent molecules agent per unit volume; B – kinetic factor, indefinite authors; $\frac{l_{cr}^{(1)}}{k_B \cdot T}$ – the relative height of the barrier free energy during of nucleus formation, this member of equation can be regarded as a parameter of stability of the material pore formation.

Detection time of the nucleus pores can be represented as

$$\tau_o = \overline{\tau_e} + \tau_r$$

where: τ_o – time of observation; $\overline{\tau_e}$ – average waiting time of the nucleus pore; τ_r – the relaxation time of the system due to genesis pores.

Since the frequency occurrence of nucleuss of the number of the nucleus, which arose in the unit observed time

$$\bar{\tau}_e = \frac{n_{pores}}{N_1 \cdot B \cdot e^{-\frac{I_{cr}^{(1)}}{k_B \cdot T}}} - \tau_p$$

In this equation, the unknown is a kinetic factor that must be found empirically.

Conclusion

Conditions are found of equilibrium gas blowing agent in the porous material (equation (2)).

Found gas pressure agent blowing agent inside the closed pores are spherical in an equilibrium state (equation (4)). The greater the difference between the chemical potentials systems material pore, the lower the pressure will be in the gas inside the pores. Because convective heat transfer in a gas is directly proportional to the pressure, then this statement can be paraphrased as follows: to achieve the minimum heat transfer pores necessary to increase the difference the chemical potentials of the systems, material-pores.

We find the critical radius of the nucleus pores. It is proved that the existence of pores is necessary that $\varphi^{(1)} - \varphi^{(1pre)} < 0$ and $r > r_{cr}^{(1)}$. At the same time critical radius is directly proportional to the surface tension. Time in the initial mixture is more likely to occur in areas with low surface tension (data field can be formed by fluctuations of density).

Works found pore formation, as well as average waiting time pores.

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