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Modelling the process of interaction of porous titanium adsorbent with a multi-component gas environment

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Abstract. A model of mass transfer of two-component gas through an absorbing porous body was developed. The mathematical model is a problem of Stefan problem type. Analytical solutions of the model in the quasi-stationary regime were obtained. For the transfer of nitrogen-oxygen mixture by titanium porous adsorbent, the dependences of the gas penetration depth and the mass absorbed by the adsorbent on the temperature, the pressure of the gas mixture and the diameter of the porous material particles were calculated. It was found that the size of the nitrogen absorption area was several times smaller than the size of the oxygen absorption area. Also, the mass of the absorbed nitrogen was half the mass of the absorbed oxygen. This is due to the remoteness of the nitrogen absorption area from the outer surface of the titanium adsorbent.

1. Introduction

The interaction of porous materials, in particular, titanium, with the components of the gas medium, is important in the sintering processes of powder materials, in the heat treatment of porous materials, in their diffusion welding, in the purification of inert gases from active impurities by porous adsorbents. In all the cases, the result of the interaction is a change in the physical and chemical characteristics of the porous titanium material and its properties. Such changes can be both the goal of the process and a negative factor hindering its implementation. In both cases, the actual task is to predict the development of these processes. The possibility to forecast the result allows one to design rational technological operations of processing porous titanium materials, to estimate the resource of effective use of fine filters. Due to the complexity of the experimental study of the interaction of porous titanium with active components of a multicomponent gas medium, the main method of analysis is the modeling of processes.

2. Actuality

The physical-chemical and microstructural state of the contact surfaces and volume of porous titanium materials are determined by the development of interaction with active gas impurities of the protective media. Currently, one can find data on the processes of oxidation and nitriding of titanium, both at atmospheric and at low pressures [1-5]. For simple titanium, these processes were studied for single-component media [6-8], without taking into account the actual composition of the protective medium or residual gases during vacuuming. At the same time, the mechanism and kinetics of the processes of

oxide formation, nitride and gas-saturated layers in the conditions of the competition of adsorption processes in the pore channels remain unstudied. Features of the transfer of multi-component gases in the channels of the porous adsorbent require the development of existing models [9-14] of such processes. In this paper, this problem was solved by the example of the interaction of a multi-component gas medium with a porous titanium adsorbent.

3. Problem statement

Nitrogen and oxygen are gas medium components which are interacting with titanium most actively. Therefore, we will limit ourselves to consideration of the process of transfer and absorption of a nitrogen-oxygen mixture from ambient air into the porous titanium adsorbent. We will use the following simplifications that are reasonable for a process conducted at high temperatures.

1. In the depth of the titanium adsorbent, an area with ultra-low nitrogen and oxygen pressure is formed (self-evacuated zone [5,6]). We assume the gas pressure to be zero in this zone.

2. In the rest of the adsorbent (transfer zone), the transfer is carried out according to Darcy law [16].

3. Oxygen actively displaces nitrogen in the interaction with titanium [1–4]. Therefore, the transfer zone is divided into two areas: area I of oxygen absorption adjacent to the outer surface of the adsorbent, followed by area II of nitrogen absorption.

4. As numerous experimental results show [1–3], the absorption rate of nitrogen and oxygen by titanium is independent of the gas pressure over a wide range of pressure values. Therefore, in the transfer zone, the absorption constants for these gases are considered independent of the pressure of the components.

5. The interaction of oxygen and nitrogen with titanium is accompanied by their active dissolution in the volume of titanium. This leads to self-cleaning of the titanium surface from oxides and nitrides [3]. Therefore, the boundary between areas I and II is considered to be mobile.

6. The pressures at which the mean free path of the gas molecules exceeds the pore diameter are considered, so the gas is transferred into the molecular condition [9]. In the same approximation, the transfer of the gas components is considered to be independent.

7. At high temperatures the rate of gas absorption by titanium is much higher than the rate of change in the gas concentration in the pore volume, so a quasi-stationary approximation is used to describe the transfer [9]. In this approximation, the rate of change in the volume concentration of gas components is neglected.

The resulting scheme of the changes in the concentration of oxygen (n_1) and nitrogen (n_2) in the coordinate x measured from the outer surface of the titanium adsorbent is shown in figure 1.
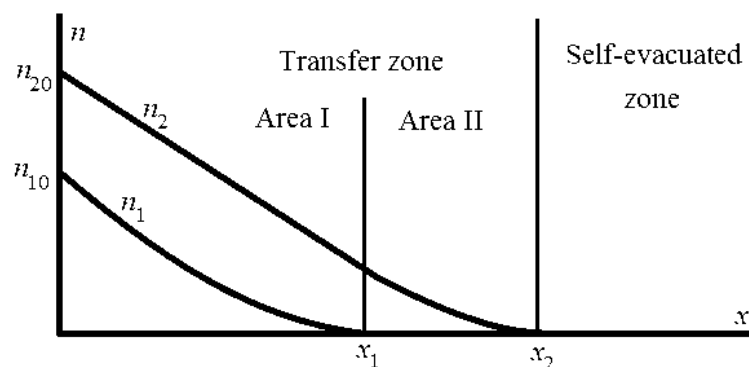

Figure 1. The concentration distribution of the absorbed components of the gas along the direction of transfer.

Next, we formulate a mathematical model of the transfer process within the framework of the assumptions made.

4. Theoretical part

Let us write the equation of the oxygen and nitrogen transfer in the titanium adsorbent.

The oxygen transfer and absorption occurs only in area I (figure 1) and is described by the quasi-stationary equation of diffusion type [9]

$$D_1 \frac{\partial^2 n_1}{\partial x^2} = \frac{\alpha \rho K_1}{\sqrt{t - t_1(x)}} \theta\big(t - t_1(x)\big), \quad 0 < x < x_1(t) \tag{1}$$

Here D_1 is the effective diffusion coefficient of oxygen in a porous medium proportional to the filtration coefficient, α, ρ are the specific surface area and density of the titanium porous adsorbent correspondently, K_1 is the constant of absorption of oxygen by titanium [1-4], $x_1(t)$ is the boundary coordinate of the oxygen transfer area (figure 1), and $t_1(x)$ is the inverse function to $x_1(t)$, $\theta(x)$ is the unit step function.

The boundary conditions to equation 1 are the given oxygen concentration n_{10} in the external environment and the conditions of agreement at the boundary of the oxygen absorption area:

$$n_1(0,t) = n_{10}, \ n_1(x_1,t) = 0, \ \frac{\partial n_1}{\partial x}(x_1,t) = 0 \tag{2}$$

The nitrogen transfer in area I occurs without absorption, therefore, in the quasi-stationary approximation, the distribution of the nitrogen concentration is described by a linear function. As a result, we get the relation

$$\frac{n_2(x_1,t) - n_{20}}{x_1} = \frac{\partial n_2}{\partial x}(x_1,t) \tag{3}$$

This relation is a boundary condition for the transport equation in area II. In this area, the nitrogen is absorbed by the titanium, and similarly to equation 1 we have the equation

$$D_2 \frac{\partial^2 n_2}{\partial x^2} = \frac{\alpha \rho K_2}{\sqrt{t - t_2(x)}} \theta\big(t - t_2(x)\big), \quad x_1(t) < x < x_2(t) \tag{4}$$

The meaning of the notation is similar to that in equation 1. Here $x_2(t)$ – the coordinate of the boundary of the nitrogen transfer area (figure 1). At this point the boundary conditions to equation 4 are

$$n_2(x_2,t) = 0, \ \frac{\partial n_2}{\partial x}(x_2,t) = 0 \tag{5}$$

In equations $1 - 5$, functions $x_1(t)$, $x_2(t)$ are not set. These functions should be determined by the solution of the problem. Therefore, the problem is nonlinear (Stefan-type problem) and should be solved by special methods.

The solution of the problem in equations $1 - 2$ is given in [13]. The result of the solution is written in the form

$$x_1(t) = \sqrt{A_1 \sqrt{t}}, \quad A_1 = \frac{4}{\pi} \frac{D_1 n_{10}}{\alpha \rho K_1}$$

(6)

and the concentration distribution is expressed by an approximate self-similar formula

$$\frac{n_1}{n_{10}} = (1-\xi)^{3/2}\left[1 - \left(1 - \frac{8}{3\pi}\right)\xi\right], \quad \xi = \frac{x}{x_1(t)}$$

(7)

The obtained solution (equation 6) appears in the boundary condition equation 3. In equations 3 – 5, the function $x_1(t)$ is given, and $x_2(t)$ – unknown. We will solve equations 3 – 5 with a method similar to that used to solve equations 1 – 2.

We integrate equation 4 with respect to the x-coordinate using the second condition in equation 5:

$$\frac{\partial n_2}{\partial x}(x,t) = -\frac{\alpha \rho K_2}{D_2} \int_x^{x_2} \frac{dx'}{\sqrt{t - t_2(x')}}$$

(8)

We further integrate equation 8 for the x-coordinate using the first condition in equation 6 and change the order of integration in the repeated integral

$$n_2(x,t) = \frac{\alpha \rho K_2}{D_2} \int_x^{x_2} \frac{(x'-x)dx'}{\sqrt{t - t_2(x')}}$$

(9)

We use expressions equation 8 and equation 9 in the boundary condition equation 3. As a result, we obtain the integral equation for the function $x_2(t)$:

$$\int_{x_1}^{x_2} \frac{x'dx'}{\sqrt{t - t_2(x')}} = \frac{D_2 n_{20}}{\alpha \rho K_2}$$

(10)

We will look for the solution of equation 10 in the form similar to equation 6:

$$x_2(t) = \sqrt{A_2 \sqrt{t}}$$

(11)

Substituting equation 11 and equation 6 into equation 10, we obtain the transcendent equation for the determination of the constant A_1:

$$\frac{A_1}{A_2} = \cos\left(\frac{\pi}{2}\zeta\frac{A_1}{A_2}\right), \quad \zeta = \frac{D_2 n_{20} K_1}{D_1 n_{10} K_2}$$

(12)

It is easy to see that equation 12 always has a unique solution with $A_2 > A_1$. Using the expansion of the cosine into the Taylor series, one can obtain an approximate solution of equation 12:

$$A_2 = \frac{1}{2}\left(1 + \sqrt{1 + \frac{\pi^2 \zeta^2}{2}}\right)A_1$$

(13)

Finally, the distribution of the nitrogen concentration in area II is given by the formula of the equation 7 form, where $\xi = x / x_2(t)$.

Next, we find the mass of components absorbed by the unit area of the adsorbent. To do this, we integrate the source densities from equation 1 and equation 5 along the length of the absorption area of the corresponding component and then using solutions equation 6 and equation 11. As a result, we obtain the masses of the absorbed oxygen M_1 and nitrogen M_2:

$$M_1(t) = \varphi(0)\alpha\rho K_1 \sqrt{A_1}\, t^{3/4}, \quad M_2(t) = \varphi\left(\sqrt{\frac{A_1}{A_2}}\right)\alpha\rho K_2 \sqrt{A_2}\, t^{3/4}$$

(14)

where the function $\varphi(z)$ is determined by the integral

$$\varphi(z) = \frac{2}{3} \int_0^{\sqrt{1-z}} \frac{dt}{\left(1-t^2\right)^{3/4}}$$

(15)

and $\varphi(0) \approx 1.748$. Let us analyze the obtained solution.

5. Discussion

We make calculations using the formulas equation 6, equation 11, equation 14 for the titanium adsorbent obtained by pressing the titanium powder particles of spherical shape with a diameter of d. In this case, the parameters of equation 1, equation 5 – the effective diffusion coefficient and specific surface area – can be expressed in terms of a particle diameter and porosity of the material [15,16].

To calculate these, we use the experimentally measured values of the absorption constants [1-4]

$$K_1 = 230 e^{-\frac{172500}{RT}} \left[\frac{g}{sm^2\sqrt{s}}\right], \quad K_2 = 15 e^{-\frac{137100}{RT}} \left[\frac{g}{sm^2\sqrt{s}}\right]$$

(16)

Here R is the universal gas constant, and T is the absolute temperature.

The calculations were carried out for the temperature range of 800–1000°C, the air pressure range of 10^2–10^5 Pa, the range of the particle diameters of 1–100 μm, the duration of the time interval of 1 hour and the porosity of the adsorbent of 20%.

The results of the calculation of the oxygen and nitrogen penetration depth dependence on the temperature and particle diameter are shown in figure. 2.

The results of the calculation of the absorbed mass of the components depending on the temperature and pressure are shown in figure 3.

It should be noted that in the calculations, the absorbed mass was independent of the diameter of the adsorbent particles at a fixed porosity.

The obtained numerical results are in agreement with the available experimental data on the penetration of residual gases into a porous titanium billet [5].
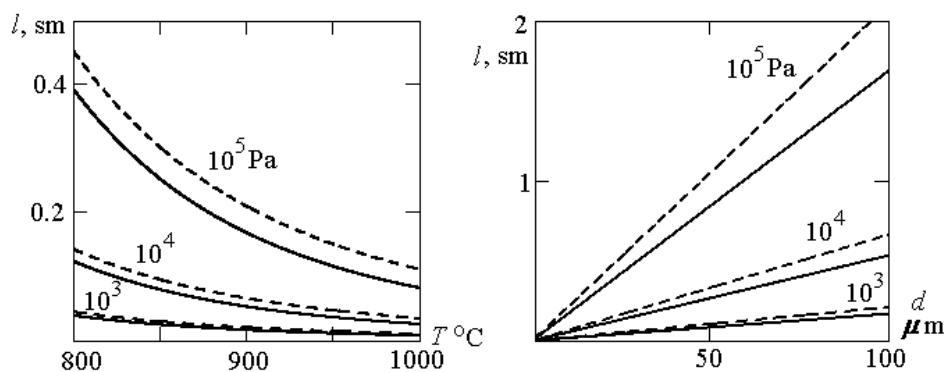
Figure 2. The dependence of the depth of the oxygen (solid lines) and nitrogen (dashed lines) penetration on the temperature at $d = 10$ μm and on the particle diameter at 900°C and different pressures.
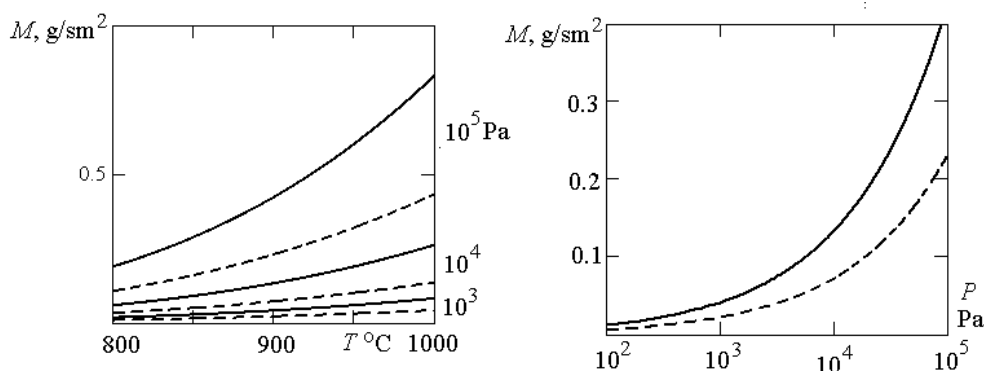

Figure 3. The dependence of the absorbed mass of the oxygen (solid lines) and nitrogen (dashed lines) on the temperature at $d = 10$ μm and on the pressure at 900°C.

It can be seen from figure 2 that the size of the nitriding area is several times smaller than the oxygen absorption area. This is due to the fact that the nitrogen flow has an additional hydrodynamic resistance due to the need to overcome the oxygen absorption area. For the same reason, the mass of absorbed nitrogen is about half that of the oxygen one (figure 3). This conclusion was confirmed by the control calculation for the transport of pure nitrogen, in which the penetration depth and absorbed nitrogen mass increased to the level observed for oxygen.

6. Summary
To describe the process of transfer of multi-component gas in the porous titanium adsorbent, a mathematical model was constructed, which uses experimentally measured parameters of the pore structure-specific surface area, filtration coefficient, porosity. The analytical solution of the model for isothermal conditions was obtained. The adequacy of the model to the available experimental data was shown.

References
[1]   Kiparisov S S and Levinskij Yu V 1972 *Nitriding of refractory metals* (Moscow: Metallurgy)
[2]   Vojtovich R F, Golovko E I 1984 *High-temperature oxidation of titanium and its alloys* (Kiev: Scientific Thought)
[3]   Peshkov V V, Podoprikhin M N, Voroncov E S and Miljutin V N 1984 On the high-temperature interaction of titanium with residual gases of the vacuumed space *Russian Jornal of Non-Ferrous Metals* vol 1 pp 41-44
[4]   Kireev L S, Selivanov V F, Peshkov V V 1994 Interaction of titanium with gases at heating in the nitrogen environment *Metal science and heat treatment* vol 6 pp 12-16
[5]   Kireev L S, Selivanov V F, Peshkov V V 1997 Physics and chemistry of the process of diffusion bonding of porous-monolithic titanium-based metal-ceramic products *Welding and Surfacing Reviews* 9 vol 1
[6]   Bataronov I L et al. 2010 Modeling mass transfer in the system of highly absorbing pore canals *Control systems and information technology* vol 42 №4 pp 49-52
[7]   Bataronov I L et al. 2014 Regularities of the mass transfer in a porous absorbent material *Bulletin of Voronezh state technical university* vol 6 № 12 pp 9-10
[8]   Bataronov I L Selivanov V F Selivanova A V 2014 Integral and differential parabolic model of

the mass transfer in an absorbing porous medium *Bulletin of Voronezh state technical university* vol 10 № 4 pp 74-77

[9]   Bataronov I L, Petrenko V R, Peshkov V V 2006 Physical and mathematical modeling gas flow through technological gaps of variable cross-section during diffusion welding *Bulletin of Voronezh state technical university* vol 2 № 6 pp 5-12

[10]   Bataronov I L, Islent'ev O V, Petrenko V R, Peshkov V V, Selivanov V F 2009 Modeling two-dimensional flows with singular absorption by the feature extraction method *Control system and information technology* vol 38 № 4 pp 4-8

[11]   Bataronov I L, Islent'ev O V, Petrenko V R, Selivanov V F, Balbekov D N 2011 Modeling the heat and mass transfer in slotted channels with topochemical exothermic reactions *Bulletin of Voronezh state technical university* vol 7 № 2 pp 4-6

[12]   Bataronov I L et al. 2013 Regularities of the gas transfer in absorbing contact gaps *Bulletin of Voronezh state technical university* vol 9 № 2 pp 138-141

[13]   Bataronov I L, Peshkov V V, Selivanov V F, Islent'ev O V 2014 Modeling the mass transfer in an absorbing vacuum-processed cavity during heating *Bulletin of Voronezh state technical university* vol 10 № 1 pp 66-70

[14]   Kurig H, Russina M, Tallo I, Romann T, Lust E 2016 Suitability of an infinite slit-shaped pore model to describe the pores in highly porous carbon materials *Carbon 100* pp 617-624

[15]   Dietrich P et al. 2015 Flow and transport in fractured porous media *Springer-Verlag* (Berlin)

[16]   Masket M 2004 Flow of homogeneous liquids in a porous medium *Institute of computer research*