The water outgassing rate of internal surfaces of vacuum systems

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Abstract. On the basis of experimental adsorption isotherm the ratio between the real and geometrical surfaces was calculated and the amount of gas required to form a monolayer was defined. Simultaneous usage of Henry and Frendlih equations allowed to determine the dependence of the heat of adsorption on the logarithm of the absorbed gas amount A mathematical model of pumping of the vacuum systems with adsorbing walls is presented. This model uses the parameters of the vacuum system and the dependence of the adsorption heat on the amount of the adsorbed gas .The conditions of the existence of regular pumping regime are discussed. The structure database vacuum adsorption properties of materials was proposed. The experimental data on the determination of the adsorption outgassing rate were released.

1. Introduction

Adsorption outgassing from internal surfaces of vacuum systems is the main component of the gas load in unheated vacuum systems. It is associated with desorption of water vapor adsorbed from the atmosphere of vacuum chamber during depressurization. There are diffusion [1] and the adsorption [2] models of outgassing in vacuum systems. This work is devoted to the discussion of the adsorption model. The work [2] is proposed to use the Temkin's isotherm equation with the linear dependence of the heat of adsorption on the amount of adsorbed gas.

This work describes adsorption model based on Frendlih's isotherm equation that describe the experimental curves well. Experimental curves of outgassing published in the works [1–3, 9] for the same materials, differ within an order of magnitude and are suitable for the calculation of gasload for vacuum systems, whose parameters are similar to the experimental units, in which the coefficients of outgassing were determined. In this work for calculating of outgassing rates we are taken into account the gas adsorption properties of the surface and the parameters of the vacuum system. This model is the base of method of forming the database to determine the rates of adsorption outgassing of different vacuum settings.

2. The composition of the surface

The basic material for manufacturing of vacuum chambers is a non-magnetic austenitic stainless steel. Aluminum alloys are used less and titanium alloys are used seldom. The elemental and quantitative composition of the stainless 12X18H10 surface before and after ion etching was analyzed by the photoelectron spectrometer Thermofisher Scientific Escalab 250Xi .The parameters of first etching cycle of surface were: energy of argon ions 3000 eV, spot's diameter: 1 mm, etching time: 10 s, the

angle between the surface normal and the direction of the incident ions – 40°; in second cycle of etching the time was increased to 60 s. The results of the elemental composition of the surface are shown in table 1.

Table 1. Elemental composition of the surface.

Element	% of atoms		
	Before etching	After 1 cycle of etching	After 2 cycles of etching
C	48.49	–	–
O	44.42	26.79	5.80
Cr	4.76	19.87	20.07
Ni	–	6.89	7.35
Ca	1.51	–	–
Fe	0.82	46.44	66.78

A large amount of carbon before the first etching cycle indicates sample contamination. The composition of the main component of steel 12X18H10T in table after the second cycle of etching, in general, coincides with the volumetric composition of the steel. A noticeable amount of oxygen on the surface may indicate the oxide presence. The results imply that for untreated stainless steel the adsorption of water vapor occurs on the surface polluted by carbon. After cleaning the surface adsorption takes place largely on the oxides. The results are confirmed by the data in work [9].

3. Adsorption isotherms

The adsorption isotherm on untreated stainless steel (R_a = 17 μm, T = 298 K) in the pressure range $1…10^3$ Pa determined by volumetric method as in work [6] is well described by Frendlih equation:

$$a(p) = 1.85 \cdot 10^{-2} p^{0.34}, \tag{1}$$

where a – the specific amount of adsorbed gas, m^3Pa/m^2; p – pressure of water vapor, Pa.

The adsorption isotherm on electropolished stainless steel at T = 310 K determined by dynamic method [4], in the pressure range of 10^{-2}–10^{-8} Pa is well-described by Frendlih equation:

$$a(p) = 1.76 \cdot 10^{-2} p^{0.25}. \tag{2}$$

Electropolishing leads to decreasing the pressure exponent.

4. The surface structure

The real surface of the vacuum chamber is not smooth. It has roughness, cracks and other defects. The relation between the real and the geometric surface may be determined using BET adsorption isotherm [5]. Considering that at the smooth surface can be placed $4.9 \cdot 10^{18}$ $1/m^2$ of water molecules, we found that the real surface of the raw stainless steel is bigger in 5.8 times than geometric surface. We assume that the water condensation probability $s = 1$.

5. The heat of adsorption

Henry and Frendlih isotherm equation gave similar results over a wide range of pressures if a linear dependence of the heat of adsorption on the logarithm of the amount of absorbed gas exists:

$$Q_a = Q_1 - K_Q \lg(a), \tag{3}$$

where $Q_1 = RT \ln\left(\dfrac{d^{1/m}}{K \cdot \tau_0}\right)$; $K_Q = \dfrac{RT(1-m)}{0.43 \cdot m}$.

According to equation (1) for water on the stainless steel: $d = 0.0185$; $m = 0.34$. At $\tau_0 = 1.6 \cdot 10^{-13}$ s and $K = 147.5$ we receive that $Q_1 = 3.15 \cdot 10^7$ J/kmol and $K_Q = 1.12 \cdot 10^7$ J/kmol.

6. The model of pumping of vacuum chamber with adsorbing walls

Without pumping of vacuum chamber ($q_p = 0$) (figure 1) processes of evaporation q_e and condensation q_c of gas molecules occur at the free surface simultaneously.
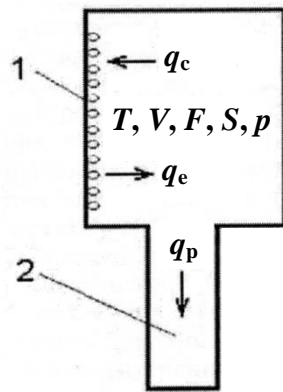

Figure 1. The model of pumping of the vacuum chamber with absorbing walls: 1 – vacuum chamber; 2 – the vacuum pump.

For pumping water vapor at 298 K in vacuum systems equation $a = dp^m$ of Frendlih's adsorption isotherm can be used. Adsorption outgassing rate will be determined by the formula

$$q_a = -\frac{da}{dp} \cdot \frac{dp}{dt} = \frac{d \cdot m \cdot S \cdot p^m}{V + F \cdot d \cdot m \cdot p^{m-1}}. \tag{4}$$

The model of pumping vacuum chamber with adsorbing walls can be presented:

$$a = d \cdot p^m; \quad \frac{dp}{dt} + \frac{S \cdot p}{V + V_\partial} = 0;$$

$$V_d = F \cdot m \cdot d \cdot p^{m-1}; \quad q_a = \frac{d \cdot m \cdot S \cdot p^m}{V + F \cdot d \cdot m \cdot p^{m-1}}; \tag{5}$$

$$S = K_e \cdot S_m \left(1 - \frac{p_m}{K_e p}\right).$$

The results of calculations on the (5) at $T = 298$ K; $M = 18$ kg/kmol; $s = 1$; $d = 0.0185$; $m = 0.34$; $V = 1$ m^3; $F = 10$ m^2; $S_m = 0.2$ m^3/s; $p_f = 10^{-8}$ Pa; $p_s = 10^3$ Pa and $K_e = 1$ give the graphs on the time (figure 2).
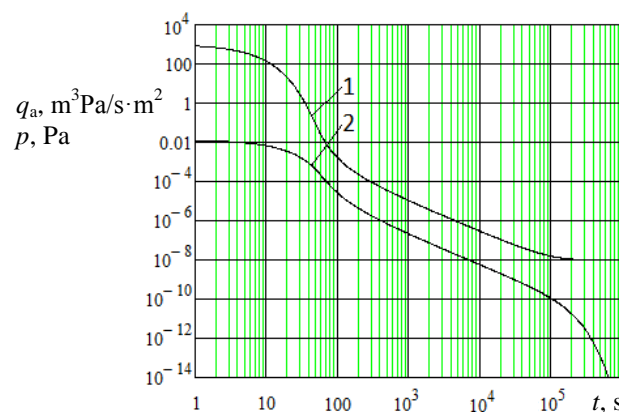

Figure 2. Dependence of pressure (1) and outgassing rate (2) of vacuum system on pumping time.

7. Dependence of the adsorption outgassing rate on pumping time and parameters of vacuum system

Adsorption outgassing rate during pumping of the vacuum chamber in accordance with equations (5) depends on coefficients of the adsorption isotherm and parameters of the vacuum system. The equations for regular mode depend only on the surface area and the effective pumping speed of chamber. They can be obtained by integrating (4) and neglecting the factors depending on the volume of the chamber, initial and ultimate pressures. Regular mode in figure 2 is executed at pumping times in range 10^2–10^5 s.The dependence of the pressure on the pumping time in the regular mode is as follows:

$$p(t) = \left[\frac{d \cdot m \cdot F}{S(1-m)t} \right]^{\frac{1}{1-m}}. \tag{6}$$

The dependence of the adsorption outgassing rate on pumping time in regular mode has the form:

$$q_a(t) = \frac{S \cdot p(t)}{F} = \left(\frac{F}{S} \right)^{\frac{m}{1-m}} \left[\frac{d \cdot m}{(1-m)t} \right]^{\frac{1}{1-m}}. \tag{7}$$

8. The database of adsorption properties of vacuum materials

The database of adsorption properties of vacuum materials may be composed of the coefficients d and m of Frendlih's isotherm equation (table 2).

Table 2. The adsorption outgassing rates of water vapor at $T = 298$ K.

Material	Preliminary processing	d,[m^{3}Pa]m^{-2}Pa^{-m}	m	Reference
Stainless steel X18H9T	Without processing	0.0185	0.34	This work
	Electropolishing	0.0176	0.25	[4]

The calculations in regular mode (7) except d and m from table 2 should be completed by the parameters of vacuum system (F, S).

For example, when $F_c = 10$ m^2, $S = 0.2$ m^3/s after 1 hour of pumping the specific outgassing rate according the equation (7) is equal to $2.3 \cdot 10^{-7}$ m^{3}Pa/(s·m^2). The value $m = 0.34$ (table 2) is confirmed by our experiments and works [1, 9].

5. Conclusions

Untreated stainless steel surface is polluted by carbon. Real surface is 5.8 times bigger than geometrical one. Water adsorption isotherm is described by Frendlih equation with parameters $d = 0.0185$ and $m = 0.34$. The proposed mathematical model in regular regime complies experimental results.

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