

GAS EXCHANGE IN A CLOSED VOLUME DURING VAPOR CONDENSATION

A. V. Kondratov and A. A. Potapenko

UDC 536.422.4

A differential equation describing the change in the density of residual gas inside a closed volume in the course of vapor condensation is derived and analyzed. The concentrations of gaseous-impurity atoms in the condensate obtained by the closed-volume method and in an "open" vacuum are estimated.

In the manufacture of electrovacuum apparatuses and in the vacuum spraying of films, when a material is vaporized and its vapor condensed, there occurs a "getter" effect, in which some of the atoms of the gaseous medium are enclosed and trapped within the condensate.

We estimate the concentrations of residual gas atoms trapped during the condensation of vapor in an "open" vacuum and in a closed volume. If the accommodation coefficient α ($0 \leq \alpha \leq 1$) on the condensation surface is known, then from known relations [1] it is easy to obtain an expression for the concentration of gaseous-impurity atoms n_0 trapped by the condensate in an "open" vacuum:

$$n_0 = \frac{1}{4k_0} \left(\frac{8RT_1}{\pi M} \right)^{\frac{1}{2}} \alpha \frac{P_1}{T_1} \cdot \frac{\tau_s}{h}. \quad (1)$$

We consider the dynamics of gas exchange in a closed volume, taking the example of a closed crucible.

Modern closed crucibles take the form of a separable graphite [2] or quartz [3] cylinder, in the inner cavity of which are placed the substrate and the material to be vaporized, the necessary temperature field in the crucible being achieved by means of heaters and screens. To permit evacuation of the gas from the closed crucible, its casing is permeable to the atoms of the residual atmosphere. Before spraying, the closed crucible containing the substrate and the material to be vaporized is placed in the chamber of a spraying installation. Then evacuation and degassing of the crucible is carried out. After a working pressure of the order of 10^{-5} torr has been established in the chamber of the vacuum equipment and inside the crucible, the substrate is brought to the required temperature and vaporization of the starting material begins.

We compare the integral concentrations of residual gas atoms enclosed within the film in the course of condensation inside the closed crucible and outside it (for otherwise identical conditions), disregarding gaseous impurities adsorbed on the substrate surface, which may also cause contamination of the material of the condensed thin layer. In developing a model of gas exchange, it is assumed that the chamber of the spraying apparatus has infinitely large volume and that the specific density of the gas in it ρ_1 and the temperature T_1 are constant over time. In this model, the conduction of the pores and the manufacturing flaws in the walls of a real closed crucible of volume V is replaced by an equivalent, in the form of two channels with opposed unidirectional conduction of magnitude U_1 (from the outer chamber to the closed volume) and U_2 (from the closed volume into the chamber), the cross-sectional area of each of the channels being denoted by F .

We assume that the law of thermomolecular flow is valid both in the real structure and in the model [1], so that

$$\frac{U_2}{U_1} = \sqrt{\frac{T_2}{T_1}}. \quad (2)$$

Agrophysical Scientific-Research Institute, Leningrad. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 29, No. 6, pp. 994-999, December, 1975. Original article submitted September 24, 1974.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.

In order to take account of the "getter" effect, a third channel with equivalent conduction U_c is introduced in the model. By analogy with [1]

$$U_c = U_2 \frac{aF_c}{kF}. \quad (3)$$

For comparison of the closed-volume method with condensation in an "open" vacuum, it is assumed that the accommodation coefficients of the residual gas atoms on the condensation surface in the two cases are equal.

From the kinetic theory of gases it follows that the integral concentration of gaseous impurities in the film prepared by the closed-volume method is given by

$$n_3 = \frac{1}{h} \int_0^{\tau_s} a v d\tau. \quad (4)$$

Knowing the concentration of gaseous atoms in unit volume n_2 and their arithmetic-mean velocity v_2 , we determine v from the formula [1]

$$v = \frac{n_2 v_2}{4}. \quad (5)$$

By analogy with the known relation in [1], we write the expression for the concentration of residual gas atoms inside the closed crucible for any given instant τ in the form

$$n_2 = \frac{1}{k} \cdot \frac{P_1}{T_1} \cdot \frac{\rho_2}{\rho_1}, \quad (6)$$

where ρ_2 is the specific density of the gas inside the closed crucible, depending on the time τ .

We now write the mass-balance equation for the period of vapor condensation:

$$V d\rho_2 = U_1 \rho_1 d\tau - U_2 \rho_2 d\tau - U_c \rho_2 d\tau. \quad (7)$$

The parameter characterizing the degree of hermeticity of the closed-crucible casing

$$m = \frac{U_1}{V} \quad (8)$$

can reasonably be called the "rate of inflow" of the gas into the closed volume. Introducing the notation

$$y(\tau) = \frac{\rho_2(\tau)}{\rho_1}, \quad (9)$$

$$\theta = \frac{aF_c}{kF} + 1, \quad (10)$$

we can rewrite Eq. (7) in standard form,

$$\frac{dy}{d\tau} + m\theta \sqrt{\frac{T_2}{T_1}} y = m. \quad (11)$$

If we solve Eq. (11) for the case when the gas temperature inside the closed volume, the temperature of the condensation surface, and the substrate temperature are equal to T_2 and do not change with time, then, substituting from Eqs. (9), (6), and (5) into Eq. (4) and integrating, we obtain

$$n_3 = \frac{n_0}{\theta} \left\{ 1 + \frac{1}{m\tau_s} \left(\frac{\rho_2(0)}{\rho_1} - \frac{1}{\theta \sqrt{\frac{T_2}{T_1}}} \right) \left[1 - \exp \left(-m\theta \sqrt{\frac{T_2}{T_1}} \tau_s \right) \right] \right\}, \quad (12)$$

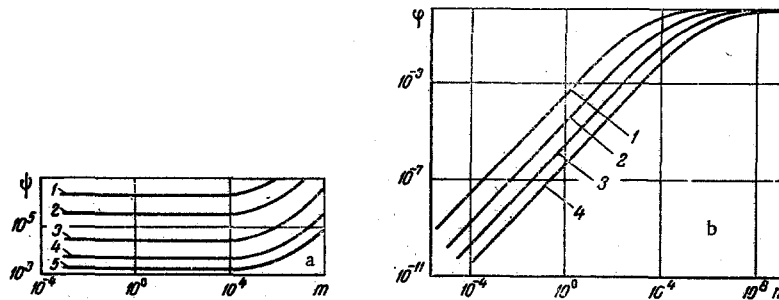


Fig. 1. Dependence of the dimensionless positive parameters φ and ψ on the inflow rate m ($T_1 = 300^\circ\text{K}$, $M = 29.89$). a: 1-5) $\alpha F_c/V = 0.564 \text{ cm}^{-1}$; 1) $\tau_s = 50 \text{ min}$, $T_2 = 300^\circ\text{K}$; 2) 5 min, 300°K ; 3) 0.5 min, 300°K ; 4) 0.05 min, 800°K ; 5) 0.05 min, 100°K ; b: 1) $\alpha F_c/V = 5.64 \cdot 10^{-4} \text{ cm}^{-1}$; 2) $5.64 \cdot 10^{-3} \text{ cm}^{-1}$; 3) $5.64 \cdot 10^{-2} \cdot \text{cm}^{-1}$; 4) $5.64 \cdot 10^{-1} \text{ cm}^{-1}$.

where $\rho_2(0)$ is the specific density of the residual gas at the instant of onset of condensation. Assuming that at the onset of vapor condensation the residual gas atmosphere inside and outside the closed volume is in a state of dynamic equilibrium, i.e., that

$$\rho_1 \sqrt{T_1} = \rho_2(0) \sqrt{T_2}, \quad (13)$$

we can rewrite Eq. (12) as

$$n_3 = n_0 f, \quad (14)$$

where

$$f = \varphi + \frac{1}{\psi} (1 - \varphi) [1 - \exp(-\psi)] \quad (15)$$

is a dimensionless function of the dimensionless parameters φ and ψ , which are related to the variables in Eq. (12) as follows:

$$\varphi = \frac{1}{\theta}, \quad (16)$$

$$\psi = m\theta \sqrt{\frac{T_2}{T_1}} \tau_s. \quad (17)$$

In Eqs. (16) and (17) the dimensions of m and τ_s are min^{-1} and min , respectively. Using the linear relation between F and m [1], we present curves of the variation of φ and ψ with inflow rate m and of the dependence of the function f on the parameters φ and ψ in Figs. 1 and 2, respectively (bilogarithmic coordinates are used). Investigating the effect of the parameter m on the solution of the differential equation describing the evacuation of residual gas from a closed crucible of fixed design, we find that the region of change of the hermeticity of the closed volume should be bounded at the left by the value $m = 10^{-2} \text{ min}^{-1}$. This means that, for smaller values of inflow rate m , the evacuation of gas from the closed crucible is difficult and takes too long. In addition, the inflow rate m must not be too large, and it is reasonable to set a bound $m = 1 \text{ min}^{-1}$ at the right, since the degassing period for the equipment and all the associated apparatuses for thermal vaporization of the material usually exceeds 30 min even in an "open" vacuum. Further, it should be noted that increase in the real condensation surface inside the closed volume without any change in its hermeticity can significantly affect the value of the parameters φ and ψ in Eqs. (16) and (17). From Fig. 2 it can be seen that for $\varphi \geq 0.5$ the advantage of the closed-volume method over spraying in an "open" vacuum is insignificant. As a result, any change affecting the value of φ should not violate the upper bound.

According to Eq. (14), the concentration of gaseous impurity in the film prepared by the closed-volume method is determined by the value of the function f . From Eq. (12) it follows that increase in hermeticity of the closed-crucible casing in the limits specified above and decrease in the time of condensation of the thin

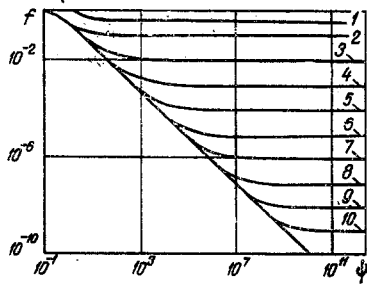


Fig. 2

Fig. 2. Dependence of function f on ψ and ϕ . 1) $\phi = 0.5$; 2) 10^{-1} ; 3) 10^{-2} ; 4) 10^{-3} ; 5) 10^{-4} ; 6) 10^{-5} ; 7) 10^{-6} ; 8) 10^{-7} ; 9) 10^{-8} ; 10) 10^{-9} .

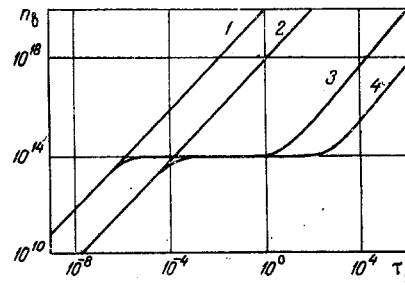


Fig. 3

Fig. 3. Effect of condensation conditions on the concentration of gaseous impurities in the film: 1) for a film (thickness $h = 3 \mu$) prepared in an "open" vacuum ($P_1 = 10^{-6}$ torr); 2) film of thickness $h = 300 \mu$; 3) film prepared in a closed crucible with an inflow rate $m = 1 \text{ min}^{-1}$ at an external pressure $P_1 = 10^{-6}$ torr ($aF_c/V = 0.563 \text{ cm}^{-1}$); 4) film prepared in a closed crucible with $m = 10^{-2} \text{ min}^{-1}$ and $P_1 = 10^{-6}$ torr ($aF_c/V = 0.563 \text{ cm}^{-1}$).

layer (for a given rate of condensation) considerably reduce the integral concentration of impurities in the film. In addition, an analysis of Eq. (14) taking into account Eqs. (15)–(17) shows that the integral concentration of gaseous impurities in the film for condensation at a constant rate by the closed-volume method gradually decreases and, for a sufficiently large thickness of the condensed layer, tends to a constant limit. This limiting value is determined by the ratio between the effective area of the condensation surface aF_c and the effective area of the pores in the closed-crucible casing kF .

A complete idea of the degree of contamination of the film material by residual gas atoms can be obtained only from an analysis of Eqs. (1) and (12). In Fig. 3 we show an example of numerical calculation by these formulas on the basis of real experimental data, from which it follows that, for low rates of condensation, the closed-volume method permits a reduction in the integral concentration of impurities in the film analogous to that achieved in an "open" vacuum on account of the decrease in residual gas pressure. In this case, the equivalent vacuum is determined mainly by the hermeticity of the closed-crucible casing and the effective area of the condensation surface of the material. Above a certain value (in our case, $500 \text{ \AA}/\text{sec}$), the condensation rate almost ceases to have any effect on the contamination of the film by residual gas atoms and, finally, for a sufficiently large rate of condensation, the contamination of the film becomes approximately the same for the closed-volume method and the "open" vacuum. However, condensation of a thin layer of material at very high rates, above $10^4 \mu/\text{sec}$, when the closed-volume method and the electric-spraying method are approximately equal in purity, involves the solution of a whole series of complex technical problems.

From these results, we conclude that, when thin films (of the order of a few microns or more) are prepared by thermal spraying in vacuo, contamination by atoms of residual gas may be sharply reduced if the process is carried out in a sufficiently hermetic ($10^{-2} \text{ min}^{-1} \leq m \leq 1 \text{ min}^{-1}$) closed crucible at a condensation rate of more than $500 \text{ \AA}/\text{sec}$. In this way, the integral concentration of gaseous impurity in films prepared by the closed-volume method can be reduced in practice to $n_3 \approx 10^{14} \text{ cm}^{-3}$, which is equivalent to the purity achieved by spraying in a superhigh vacuum.

NOTATION

n_0, n_3 , integral concentrations of gaseous impurity in the film prepared in an "open" vacuum and by the closed-volume method, respectively; a , accommodation coefficient; F_c , area of the condensation surface; F , area of the model channel connecting the outer chamber to the closed volume; π, R, k, k_0 , constant coefficients; h, τ_s , thickness and time of spraying of the film; P_1, T_1, ρ_1 , pressure, temperature, and density of the gas in the outer chamber of the apparatus; U_1, U_2 values of the conduction of the channels from the outer chamber to the closed volume and from the closed volume to the outer chamber, respectively; M , molecular weight of the gas; U_c , "carrying capacity" of the condensation surface; ν , number of atoms striking unit area of the condensation surface in unit time; V , volume of the inner cavity of the closed crucible; n_2 , number of gas atoms in unit volume inside the closed volume; v_2 , arithmetic-mean velocity of the gas atoms inside the closed volume;

ρ_2 , T_2 , specific density and temperature of the gas inside the closed volume; f , ϕ , ψ , dimensionless parameters; $m = U_1/V$, outflow rate; $y = \rho_2/\rho_1$; $\Theta = (aF_0/kF) + 1$.

LITERATURE CITED

1. S. Dushman and J. M. Lafferty (editors), Scientific Foundations of Vacuum Technique, Wiley, New York (1962).
2. Yu. Z. Bubnov, M. N. Libenson, M. S. Lur'e, and G. A. Filaretov, *Inzh.-Fiz. Zh.*, 27, No. 3 (1969).
3. I. P. Kalinkin, K. K. Murav'eva, I. B. Yurgel', V. B. Aleskovskii, and I. N. Anikin, *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, 6, No. 9 (1970).

MASS TRANSFER IN CONDENSATION OF VAPOR FROM A FLOW OF FOG-CONTAINING VAPOR - GAS MIXTURE

Ya. M. Vizel', D. I. Lamden,
and I. L. Mostinskii

UDC 536.423.4

Results are presented for the experimental settling of fog on the internal wall of a channel from a vapor-air mixture moving along it. Variation of fog concentration was determined by measurement of the intensity of scattered light. Experiment and theory are compared.

The analogy between the processes of heat and mass transfer is valid for condensation of a vapor on a cold surface from a flow of superheated or slightly supersaturated vapor-gas mixture. For a high degree of supersaturation, the intensity of mass transfer is determined not only by diffusion of vapor to the condensation surface but also by the settling of particles of condensed aerosol on it. The latter process is often predominant, and many specialists are engaged in a study of it.

The existing experimental work in this field can be divided into two groups. In the first group are studies of the settling of a fog which is formed by the artificial introduction of condensation nuclei [1, 2]. The rate of aerosol settling was determined either from the deflection of a beam of "developed" nuclei in a transparent vessel [1] or from measurements of the dust concentration introduced into the condenser and of the dust concentration emerging from it [2]. As a rule, the introduction of condensation nuclei makes it possible to distinguish in purer form the settling of an aerosol from the overall process of mass transfer during the flow of a vapor-gas mixture.

In the second group of experimental work are studies of the settling of a fog formed by homogeneous condensation of a vapor in the flow of a vapor-gas mixture. In [3, 4], the total flow rate was measured for a condensate which was formed as the result of simultaneously occurring processes of surface condensation and fog-particle settling. The relative contributions of the two processes were determined by theoretical methods only.

In the present work, a fog which was formed by homogeneous condensation before entrance into the experimental section was used as the nucleus. In this case, we measured and calculated both the total amount of condensate which settled on the wall and the variation of aerosol concentration in the flow along the condenser.

The experimental device (Fig. 1) is in the form of a closed loop through which air is pumped by the centrifugal fan 1. After leaving the fan, the air passes through the straight section 2 and the gas-flow meter 3 (for turbulent flow, this is a normal venturi; for laminar flow, it is an RS-5 rotameter). Then the air is fed into the gas heater 4, into which water vapor from the vapor generator is also fed, and into the chiller 5. The gas heater and chiller are two sequentially installed pipes with an internal diameter of 95 mm in which straight-

Institute of High Temperatures, Academy of Sciences of the USSR, Moscow. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 29, No. 6, pp. 1000-1006, December, 1975. Original article submitted July 2, 1974.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.