SURFACE DESUBLIMATION OF CARBON DIOXIDE FROM BINARY GAS MIXTURES

V. N. Shchelkunov, N. Z. Rudenko,
Yu. V. Shostak, and V. I. Dolganin

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The results of an experimental investigation of the time evolution of the main characteristics of the process of surface desublimation of carbon dioxide from N_2—CO_2 and He—CO_2 gas mixtures are given.

In choosing a means of scrubbing carbon dioxide from gases, in a number of cases preference is given to the means based on the freezing out of CO_2 onto heat-exchange surfaces. The high degree of scrubbing of gases, the high productivity, the stability of operation, and the economy of the equipment must be included among the advantages of this means.

The process of surface desublimation of CO_2, accompanied by variation of the density and thermal conductivity of the solid phase, is a combined case of heat and mass exchange with a moving boundary. In this connection, knowledge of the main laws of desublimination and the properties of the solid phase is a necessary condition for the creation of optimum constructions of freezing-out devices. An analysis of information on this problem available in the literature indicates a clear lack of such information. Only one paper is known in which data are given on the density and thermal conductivity of the solid phase of CO_2 in the early stage of its formation [1]. The remaining literature data have a particular character, since they are devoted to the study of the specifics of the operation of concrete elements of engineering systems — regenerators and recuperators of air-separating equipment.

The present paper contains the results of an investigation of the process of CO_2 desublimation in the interaction of streams of N_2—CO_2 and He—CO_2 gas mixtures with a cryogenic plate situated longitudinally. In the course of the experiments we studied the character of the time variation of the thickness, density, and thermal conductivity of the layer of CO_2 cryogenic precipitate, its surface temperature, and the densities of the convective heat and mass fluxes.

The tests were conducted on a high-pressure, cryogenic, gas-dynamic apparatus [2]. The test model was a polished copper plate 56 × 56 × 4.5 mm in size. The experimental procedure is described in detail in [3].

As visual observations and photographs showed, in all the investigated regimes the process of surface desublimation of CO_2 has a number of common features. At the initial time of $\tau < 2$ min, single crystals 0.1-0.5 mm in size, arbitrarily oriented in space, are formed on the surface of the plate. Some of the crystals are carried off from the surface of the plate by the gas stream. At subsequent times, crystal groups form around the existing crystals and the entire surface of the plate is filled up. The shapes and sizes of the crystals depend on the experimental conditions. An increase in the concentration or velocity of CO_2 diffusion in the mixture and a decrease in the plate temperature or the heat load lead to the formation of larger crystals. The most common crystal shapes are a cube, a plate, a prism, a star, and a dendrite.

In the process of formation of the solid phase of CO_2, the variation of its thickness along the plate takes place in a rather camplicated way (Fig. 1). In the first 1-2 h, despite the surface of the solid phase being practically isothermal (curve 7), the layer of cryogenic precipitate grows at a greater rate in the leading part of the plate (curve 1). This nonuniformity of thickness is connected with the depletion of carbon dioxide of the boundary layer as the mixture moves along the plate (curve 4), since diffusional transfer from its outer boundary is unable to compensate for the loss of precipitated CO_2 molecules. It should be noted that in tests with an He—CO_2 mixture, where the coefficients of interdiffusion are four times higher than in an N_2—CO_2 mixture [4], the nonuniformity of the thickness of the layer

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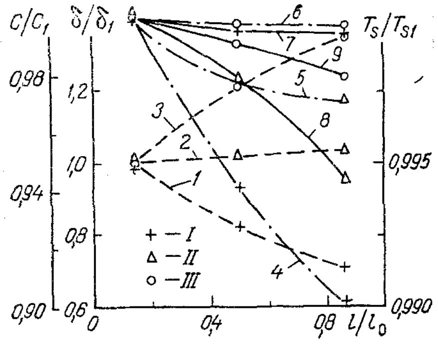

Fig. 1

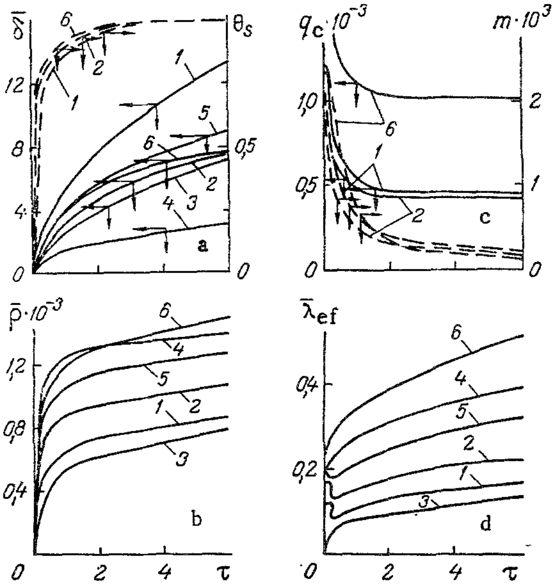

Fig. 2

Fig. 1. Distribution along the plate at different times τ of relative values of the thickness of the solid phase, its surface temperature, and the CO_2 concentration (measured at a distance of ~0.5 mm from the surface of the cryogenic precipitate) for T_∞ = 193°K, v_∞ = 3 m/sec, T_p = 145°K, P_∞ = 0.1 MPa, P_{CO_2} = 4.35 kPa, N_2–CO_2 mixture: 1-3) variation of thickness; 4-6) variation of CO_2 concentration; 7-9) variation of surface temperature; I, II, III) at τ = 1, 3, and 6 h, respectively.

Fig. 2. Time variation of the average thickness of the solid phase and its dimensionless surface temperature (a), the average density of the layer (b), the densities of the convective heat and mass fluxes (c), and the coefficient of effective thermal conductivity of the layer (d) for different experimental conditions: 1-6) from Table 1. δ, mm; $\bar{\rho}$, $kg \cdot m^{-3}$; q_c, $W \cdot m^{-2}$; m, $kg \cdot m^{-2} \cdot sec^{-1}$; $\bar{\lambda}_{ef}$, $W \cdot m^{-1} \cdot {}^\circ K^{-1}$; τ, h.

was considerably lower. As the temperature of the surface layer along the plate varies with time (curves 8 and 9), there is a redistribution of the CO_2 mass flux (curves 5 and 6) and hence a change in the rate of growth of the thickness of the solid phase. The thickness of the layer is gradually equalized (curve 2), and at τ > 4 h a higher rate of growth of the layer of cryogenic precipitate is observed in the trailing part of the plate (curve 3).

With allowance for the nonuniformity of the thickness of the layer along the plate, comprising 1-3 mm in our tests, the experimental results were compared through its average values, calculated on the basis of measurements of δ in three cross sections of the plate with coordinates l = 8, 28, and 48 mm.

In Fig. 2 we present experimental curves reflecting the time variation of the main characteristics of the process of heat and mass exchange. We note that by the terms thickness, density, and surface temperature of the cryogenic precipitate below in the text we understand their average values.

It is seen from Fig. 2a that the thickness of the layer of solid phase increases throughout the desublimation process. The temperature of the plate and the pressure of the mixture have the greatest influence on the rate of growth of the thickness of the layer. A change in the working medium from nitrogen to helium does not result in significant changes in the thickness. The law of time variation of the thickness of the layer is nearly parabolic, which agrees with the results obtained in the freezing out of moisture [5]. In this case, as follows from an examination of the δ = f(τ) and Θ_s = f(τ) curves, the highest rate of growth of the thickness of the layer occurs in the initial desublimation period, τ < 30 min, characterized by great supercooling of the surface of the layer. As the surface temperature of the solid phase increases, the rate of growth of the thickness slows. It is established that the temperature of the surface layer increases to values close to the equilibrium temperature of the CO_2 phase transition, and it subsequently grows slowly, i.e., it is practically stabilized.

TABLE 1. Experimental Conditions

Test number	T_∞, °K	T_p, °K	v_∞, m/sec	P_∞, MPa	P_{CO_2}, kPa	Mixture
1	193	118	3	0,1	4,35	N_2-CO_2
2	193	145	3	0,1	4,35	N_2-CO_2
3	193	145	0,5	0,1	4,35	N_2-CO_2
4	193	145	3	0,5	4,35	N_2-CO_2
5	199	151	3	0,1	8,76	N_2-CO_2
6	193	145	3	0,1	4,35	$He-CO_2$

Then, as local measurements of the temperature T_s show, its periodic oscillations with an amplitude of 0.2-0.5°K are observed.

The $\Theta_s = f(\tau)$ curves are well described by functions of the type

$$\Theta_s = 1 - \exp(-k\sqrt{\tau}),$$

where k is an empirical coefficient dependent on the ratio of the determining parameters and lying in the range of 1.5-3 in these tests. It was established that the velocity of the gas stream has the greatest influence on the coefficient k; an increase in the velocity leads to the simultaneous intensification of both the heat transfer to the surface of the layer and the mass transfer. Thus, $k > 2$ for $v_\infty > 3$ m/sec while $k < 2$ for $v_\infty < 3$ m/sec.

As follows from Fig. 2b, the density of the cryogenic precipitate increases with time. The solid phase becomes denser through internal diffusion – the effect of recrystallization of CO_2 molecules from "warm" sections of the layer to "cooler" sections under the action of the internal drop in the partial pressure of CO_2 due to the temperature gradient in the layer. According to the functions $\bar{\rho} = f(\tau)$ and $\Theta_s = f(\tau)$ presented, the variation of $\bar{\rho}$ correlates with the variation of Θ_s. Thus, with the increase in the surface temperature of the solid phase in the initial period, its density grows intensively, and then as the temperature Θ_s stabilizes, the layer becomes denser at a practically constant rate, indicated by the linear character of the function $\bar{\rho} = f(\tau)$. An analysis of the test data shows that high values of the density at equal times correspond to high values of P_∞, T_∞, v_∞, and P_{CO_2}. A decrease in the temperature of the plate leads to a decrease in $\bar{\rho}$, which is connected with an increase in the size and number of crystals formed, as well as with the lower density of their packing. The density of the layer is also affected by the properties of the noncondensing gas in the given process, primarily by the value of the coefficient of intediffusion. Thus, in the tests with a helium mixture the solid phase becomes denser more intensively, while the values of $\bar{\rho}$ are 1.4-1.6 times higher, other conditions being equal, than in tests with an N_2-CO_2 mixture.

The densities of the convective heat flux q_c and the mass flux m vary with time in accordance with the variation of the surface temperature of the layer (Fig. 2a, c). In the initial period, when its rapid growth is observed, the values of q_c and m fall sharply, decreasing by factors of 1.5-2.5 and 6-8, respectively, during the first 2 h. Then, with stabilization of Θ_s, the rate of change of these characteristics becomes practically constant.

The values of the coefficient of effective thermal conductivity of the layer of cryogenic precipitate calculated on the basis of our experimental data lie in the range of 0.04-0.55 $W \cdot m^{-1} \cdot °K^{-1}$. The character of the time variation of λ_{ef} for different initial conditions is presented in Fig. 2d. It is obvious that higher values of λ_{ef} correspond to higher values of the density of the layer. The rise in thermal conductivity with time is due to the change in the structure of the cryogenic precipitate as it becomes denser, since the number of contacts between crystals grows in the process. Visual observations show that in the period of intense growth of the layer the structure of the solid phase consists of a piling up of individual crystals with a large number of gas pores between them and is nonuniform over the thickness of the layer: The shape and size of the crystals vary as the surface temperature of the layer rises. As the layer becomes denser with time, the gas spaces are filled and its porosity decreases. In growing together, the crystals first form a layer with a friable structure, which is gradually converted into transparent dry ice. It should be noted that these changes in the structure of the layer take place at a nonuniform rate along the plate. Thus, the formation of transparent dry ice begins at the leading edge of the layer, gradually spreading toward the trailing edge. Abrupt increases in the coefficient λ_{ef} (curves 1, 2, and 5) are connected with a change in the mechanism of heat transfer in the early stage of the desublimation process ($\tau < 10$ min), when the layer consists of a porous structure. As the authors of [6] established, the considerable variations of λ_{ef} in this period are due to the turbulence of the gas stream because of the great roughness of the surface of the solid phase.

In summing up the analysis of the time evolution of the main characteristics of the surface desublimation of CO_2, we note the possibility of dividing the process of heat and mass exchange into two periods. The first period is characterized by considerable variations in the values of all these characteristics and is particularly nonsteady. During this period the thickness, density, and temperature of the surface layer grow rapidly, while the heat- and mass-flux densities fall. The second period can be defined as quasisteady, characterized by little time variation of the temperature of the surface layer and the densities of the heat and mass fluxes to the surface of the solid phase, whereas the thickness, density, and thermal conductivity of the layer of cryogenic precipitate continue to increase by a nearly linear law.

NOTATION

T_∞, P_∞, v_∞, temperature, pressure, and velocity of the oncoming gas stream; τ, time; P_{CO_2}, partial pressure of CO_2; T_p, plate temperature; T_c, equilibrium temperature of the CO_2 phase transition; l_0, length of the plate; l, distance from the start of the plate; δ, T_s, C, local values of the thickness of the layer of solid phase, its surface temperature, and the CO_2 concentration in the boundary layer; $\bar{\delta}$, $\bar{\rho}$, $\bar{\lambda}_{ef}$, $\bar{T}_s$, average values of the thickness, density, coefficient of effective thermal conductivity, and surface temperature of the layer of cryogenic precipitate; q_c, m, densities of the convective heat flux and the mass flux; $\Theta_s = (\bar{T}_s - T_p)/(T_c - T_p)$, dimensionless surface temperature of the solid phase. The index 1 refers to the first cross section of the plate at $l = 8$ mm.

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