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MATHEMATICAL MODEL OF DESUBLIMATION PROCESS OF VOLATILE METAL FLUORIDES

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Mathematical model for calculation of optimal temperature desublimation in metal fluorides and the number of desublimation stages has been developed; it permits achieving the degree of base product recovery from gas-vapour mixture nearly to 100 %. Experimental checking of modeling results at uranium hexafluoride desublimation shows a good correlation with the theoretical data.

Introduction

Sublimation-desublimation limit, being a refining operation is of great importance in technology of obtaining a number of pure substances and semi-products including the technology of nuclear fuel.

All existing desublimators may be divided into three groups by the way of solid phase extraction from gas flow: surface, volumetric and mixed [1]. However, all these apparatus have a significant disadvantage. It is a low yield of a main product into disublimate (80...90 %), the reason of which is aerosols formation at intense overcooling of desublimated substance vapor and their carry-over from the system. In industry the desublimation processes of ZrF_4, TiF_4, UF_6, WF_6, ReF_6 and other volatile metal fluorides are usually carried out at temperatures, which are considerably lower than actual temperatures of desublimation. The latter cause the formation of crystallization centers in apparatus volume and as a result loss of the product in the form of aerosol.

The investigations of the influence of apparatus surface temperature on desublimation process of titanium tetrafluoride carried out before showed [2], that at desublimation temperature decrease lower than the actual one by 250 °C loose desublimate of pin-fin type is formed; by 150 °C – the layer of friable product is formed; by 100 °C – solid vitreous product along the whole layer is formed. In this case products output losses from desublimator were 27, 12, and 5 wt. %, correspondingly.

The most efficient way of organizing the desublimation process would be the way at which in the conditions of changing heating rate it could be possible to suppress the process of aerosols occurrence and control the desublimator layer rise ensuring apparatus maximal filling and its passability.

1. Aerosol formation at vapor supersaturation

The point of desublimation process is in product gaseous molecules delivery from gas-vapor mixture volume to the cold desublmator surface. As far as desublimation may occur at high rate only fulfilling the condition [1]

$$S = \frac{P}{P_{\infty(T)}} \le S_{кр}, \qquad (1)$$

where S is the degree of gas-vapor mixture supersaturation; S_{cr} is the critical degree of supersaturation over which the formation process of solid phase nuclei in apparatus volume starts; P, $P_{\infty(T)}$ is the current gas pressure in the system and substance gas pressure over its desublimate at the given temperature; depending on the way of disublimation process organization various means of its behavior are possible.

If S_{cr} is obtained only on the surface of disublimate then the whole product will settle on it. In this case the lower its temperature is the higher is the rate of desublimation process. However, it is stated experimentally [2] that in this case product yield into desublimate sharply decreases due to its volumetric desublimation, always occurring there where S_{cr} is obtained, the zone of which will transfer from the surface into the volume of gas-vapor mixture (Fig. 1).

If we denote the input temperature of gas-vapor mixture into desublimator by T_1, temperature of cold surface is denoted by T_2, the distance which the gas-vapor mixture will cover having been cooled from temperature T_1 to T_2 is L then assuming that as the distance x increases from gas entry point into apparatus to its exit point the temperature of gas-vapor mixture T will decrease linearly from T_1 to T_2 we obtain

$$T = T_2 + \frac{T_1 - T_2}{L} x. \qquad (2)$$

Then pressure P will also change similarly

$$P = P_2 + \frac{P_1 - P_2}{L} x. \qquad (3)$$

Using the equations (1)–(3) the equation for determining the values of gas supersaturation degree at the preset desublimator temperature may be derived

$$S = \frac{T - T_2}{T_1 - T_2} \frac{P_1 - P_2}{P_{\infty(T)}} + \frac{P_2}{P_{\infty(T)}}.$$

In desublimators operating in working conditions gas temperatures and pressures equalizing occurs owing to turbulent and molecular diffusion and product heat conductivity. That is the processes of mass- and heat exchange – gas cooling and gas molecules carryover to desublimation surface occur simultaneously. The scheme of supersaturated vapor formation at motion of turbulent flow of gas-vapor mixture in the tube cooled outside is shown in Fig. 1 [3].

The ratio of mass and heat exchange rates is so that vapor supersaturation at the beginning increases obtaining maximal value and then decreases. In the area where it increases the critical value (shaded region) there is volumetric desublimation.

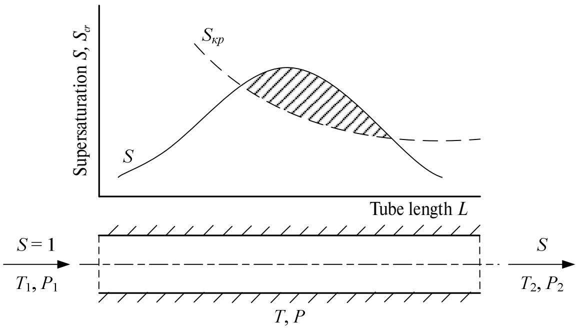

Fig. 1. *Change of vapor flow supersaturation degree when moving along the tube*

At homogeneous desublimation it is meant by critical supersaturation S_{cr} such supersaturation at which the rate of nuclei formation capable of further growth equals to a unity that is I=1 cm^{-3}·s^{-1} The similar assumption is certainly conventional as nuclei formation occurs also at I<1 but the rate of such process is low. Taking into consideration strong dependence of nuclei formation rate on vapor supersaturation [1, 3] the value of vapor critical supersaturation at its homogeneous desublimation may be calculated by the equation, taking I=1 and S=S_{cr} [3]

$$\lg S_{cr} = \sqrt{\frac{1,44}{\lg K} \frac{M}{\rho} \left(\frac{\sigma}{T}\right)^{3/2}},$$

where M is the molecular weight of desublimated substance, g/mole; ρ is the density of desublimate, kg/m^3; T is the temperature in the system, K; σ is the surface tension, J/cm^2; K is the kinetic coefficient calculated by the formula

$$K = \frac{\gamma}{\rho} \frac{2m\sigma}{\pi} \left(\frac{P}{\kappa T}\right)^2,$$

κ is Boltzmann constant equal to 1,38·10^{-23} J/K; γ is the coefficient of desublimation expressing a part of vapor molecule staying on desublimator solid surface owing to collisions (depending on desublimated substance nature, the degree of its contamination, absence of inert gas molecules and some other factors its value γ may vary from 0 to 1,0); m is the vapor molecule weight of desublimated substance, kg.

Surface stress σ is solved from the equation [3]:

$$\sigma = \frac{\Delta H - RT}{V^0} \frac{\Delta n}{n} h,$$

where ΔH is the enthalpy change at evaporation, kJ/mole; R is the universal gas constant, equal to 8,314 J/(mole·K); n is the coordination number; Δn is the number of missing neighbors of crystal lattice in surface layer; h is the thickness of molecule monolayer (for fluorides it is 0,2...0,3 nm), m; V^0 is the molar volume of solid substance, cm^3/mole, equal to

$$V^0 = \frac{M}{\rho}.$$

Certain critical size of particles meets supersaturation existing in the system at every time moment. The radius of critical spherical nucleus r_{cr} is defined from Thomson equation [3, 4]:

$$r_{cr} = \frac{2\sigma M}{\rho RT \ln S}.$$

When achieving a certain critical size (10^{-4}...10^{-3}) mkm, the nucleus stabilizes and becomes the centre of crystallization trending to unrestricted growth [3, 4]. Mass concentration of fog G, g/m^3, appearing in this case may be calculated by the equation [3]

$$G = \frac{MP_{\infty(T)}}{RT}(S - 1).$$

The question of the fact where desublimation of the product takes place – on the surface of desublimator or in the volume of gas-vapor mixture, is determined by rates ratio of mass- and heat exchange of desublimated product which may be estimated by Lewis number Le [4, 5]:

$$\mathrm{Le} = \frac{\alpha}{c_p \rho \beta},$$

where α is the coefficient of heat transfer, Wt/(m^2·K); β is the coefficient of mass transfer m/s; c_p is the specific gas heat capacity at constant pressure, J/(kg·K).

If Le>1 at the given conditions then heat exchange intensity is higher than mass transfer intensity. As a result there is not enough time for desublimating product to be delivered to desublimator surface in the form of vapor and the process of volumetric desublimation is the dominant one.

2. Desublimation process modeling

On the basis of above mentioned equations the mathematical model of desublimation process of metal volatile fluorides allowing us to calculate the multistage desublimation process and to bring the extraction ratio of target product from gas-vapor mixture almost to 100 % was developed. The mathematical model allows determining the number of desublimation stages, optimal temperature of desublimating surface at each stage excluding aerosols formation at maximal rate of desublimation process.

The results of mathematical modeling of UF_6 desublimation process are presented lower, Fig. 2, 3, as an example. So for the most complete UF_6 catching from process gas obtained at fluorination of uranium oxides the model indicated the necessity of four desublimation stages organization at 288, 267, 246 and 224 K (at these temperatures the condition $S=S_{cr}$ is fulfilled). In this case the outlet residual pressure of UF_6 in gas mixture from each stage is equal to $7{,}37 \cdot 10^3$; $1{,}38 \cdot 10^3$; $1{,}86 \cdot 10^2$ and 13,3 Pa, and its collection efficiencies at each stage are 76,05; 19,51; 3,9 and 0,5 %, correspondingly. Thus, the collection efficiency of UF_6 after four stages of desublimation forms not less than 99,96 %.

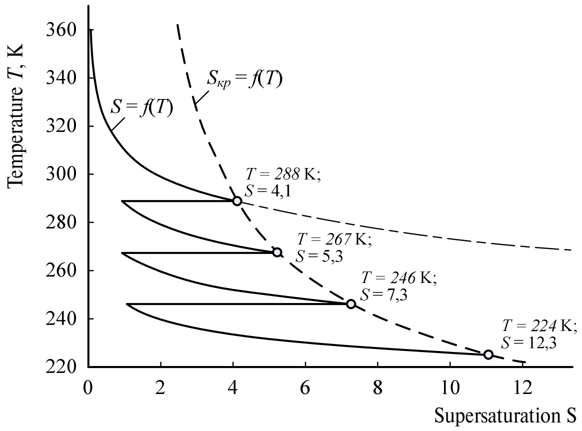

Fig. 2. *The degree of supersaturation and critical degree of supersaturation at different temperatures of desublimator wall*

At the outlet from each stage of desublimation gas containing residual pressure of UF_6 and formed aerosols is directed through the heated pipelines to the next stage of desublimation. And at organization of one stage of desublimation the degree of vapor supersaturation at temperature 224 K the degree of UF_6 supersaturation is $2{,}3 \cdot 10^3$ (dash-dot line in Fig. 2).

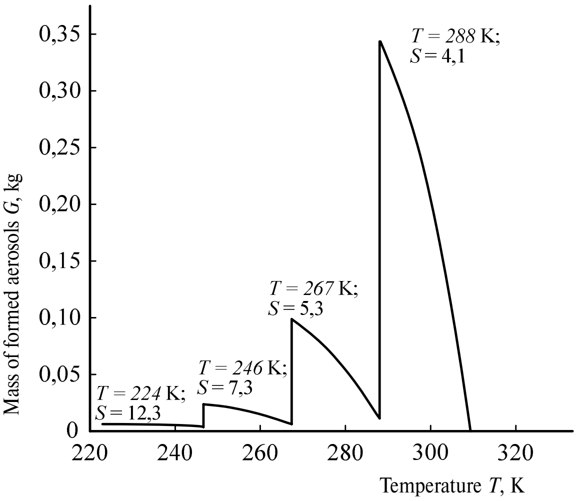

Fig. 3. *The dependence of the mass of UF_6 formed aerosols on the temperature of desublimator wall*

Conclusion

The mathematical model for calculating the efficient temperature of substances desublimation has been developed. It allows revealing those parameters of the process at which the maximal rate of surface desublimation process is achieved and the process of aerosols formation in the volume of the apparatus is minimized.

The suggested technique of calculation of desublimation process parameters is checked while determining the optimal conditions of UF_6 and TiF_4 desublimation processes and may be applied for the similar calculations of desublimation (condensation) processes of other metal volatile fluorides supporting maximal efficiency of the process.

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