Influence of radiative heat transfer on the sublimation of a single chromium (III) $\beta$-diketonate particle in the superheated mixture of vapor-inert gas

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Abstract. The paper presents the results of numerical simulation of nonstationary sublimation of spherical particles of Cr(acac)$_3$, floating in the volume of a binary mixture (argon-superheated vapor of precursor) in a reactor with hot walls. The influence of the vapor content, reactor wall temperature and radiative heat transfer on the kinetics of sublimation/desublimation are analyzed. The characteristic times of induction and total sublimation, as well as the intensity of mass entrainment from the surface of particles of different sizes are determined. The influence of radiation from the hot walls of the sublimator on these parameters is determined.

1. Introduction

For the aviation, energy gas-turbines and catalysis reactors improvement the development of new refractory oxide coatings is an important problem. As pointed out in [1-4] one of the perspective methods is a plasma- or laser-activated chemical deposition from gas phase (CVD) using volatile compounds of metals with organic ligands (MO CVD).

Growth rates of the target metal oxide film sufficient for technological processes as well as high completeness of the precursor can be achieved in processes at atmospheric and reduced pressure of a carrier gas. The necessary flow rate of precursor vapors can be provided by sublimation of the initial compound in a high-intensity vortex sublimator [3]. The peculiarity of this sublimator is the rapid transition of the precursor to the vapor state in the circulating fluidized bed of particles, floating in the carrier gas. At precursor dosing, new particles supplied in the sublimator may enter the carrier gas mixture with precursor vapors in a saturated or superheated state relative to the cold particles. The sublimator and the conveyor of precursor vapor in the reaction zone are typically heated to avoid the vapor desublimation on the walls. At high wall temperatures and low heat of the phase transition during the heating of precursor particles, heat transfer becomes significant due to radiation from the walls of the sublimator or steam line. As it was shown earlier [5], radiation heat transfer plays a key role in reactors with cold walls and allows controlling the process of sublimation of large particles of precursor Zr(dpm)$_4$ by changing the temperature of the walls.

This paper presents the results of numerical simulation of nonstationary sublimation of spherical particles of Cr(acac)$_3$, floating in the volume of a binary mixture (argon-vapor of precursor) in a reactor with hot walls. The used physical and mathematical model of the process and its verification
are presented in [2]. The model was extended to processes with a significant effect of radiation in [4]. In this paper, the influence of vapor content, reactor walls temperature and radiative heat transfer on the kinetics of precursor particles sublimation/desublimation is analyzed.

2. Problem statement and solution method

In figure 1, the scheme of the sublimation process (left), the computational domain (schematic) and the main parameters (right) are presented for diffusion sublimation in the reactor with hot walls.

In practice, sublimators have different sizes, usually less than 1 m in diameter; and solid particles of the precursor move in the fluidized bed of other particles, which limits the available space for diffusion of precursor vapor from the particle. These factors can have a significant effect on the heat and mass transfer at the particle surface, the warm-up time and the total sublimation time of the particle. In this case, the diameter of the computational domain was 1 m, and the particle size did not exceed 4 mm. This allowed excluding the influence of a limited volume on the change in composition and pressure near the particle during its sublimation.

Figure 1. The problem statement and main parameters for the case of diffusion sublimation in the reactor with hot walls.

3. Results and discussion

Consider the case of sublimation of a Cr(acac)$_3$ particle into a vapor-gas mixture at changing mass concentration of precursor vapor in argon. The initial temperature of the vapor-gas mixture is equal to the temperature of the reactor walls. Calculations are made taking into account the radiation heat transfer between the particle and the reactor walls (red lines in the figures) and regardless of it (black lines). At the initial time, the cold particle enters the vapor-gas mixture with vapor concentration exceeding that of saturated vapor for the particle at room temperature. Figure 2a shows that the diameter of the particle increases during the first 30-100 seconds, and figure 2b shows the negative intensity of sublimation (desublimation of precursor vapors on the particle) during this period of time. The specified time by analogy with the combustion of particles can be called the induction time. In terms of sublimator operation at preparation of organometallic compound vapors in the CVD process, this negative factor must be taken into account. During the induction time, the precursor particle
reduces the vapor concentration in the sublimator and the steam line. If during the induction the particle leaves the sublimation zone, for example, due to the high velocity of the carrier gas, it falls into the reaction zone, which inevitably leads to a defect in the deposited coating. Under the considered conditions, the total sublimation time was from 1000 to 3000 seconds. Thus, the induction time can be up to 10% of the total sublimation time.

![Graph of particle diameter evolution](image1)

**Figure 2.** The evolution of the square of relative particle diameter (a), the intensity of the precursor vapor entrainment from the particle surface (b), the temperature of the particle center (c) and the specific mass flux density on the particle surface (d) over time for different concentrations of precursor vapors in the medium around the particle.

Over time, the particle warms up, which leads to an increase in the saturation pressure on its surface and, accordingly, the equilibrium concentration of precursor vapors. The particle temperature reaches the maximum value at the moment of completion of the particle growth (figure 2c), the sublimation intensity becomes positive, the vapor concentration on the surface becomes higher than the concentration in the external volume, the particle begins to sublimate, slowly decreasing in diameter according to a known law \((d/d_0)^2\). As the particle diameter decreases, the specific mass flow of precursor vapor from its surface increases (figure 2d), but the surface area of the particle decreases much faster, so the mass flow (figure 2b) decreases continuously over time. Calculations taking into account the heat flux to the particle surface due to radiation show that radiation intensifies heat and mass transfer on the surface of the particle, which is expressed in a higher equilibrium temperature of the particle, a decrease in the induction time and an almost twofold increase in the mass...
flow from the surface of the particle in the sublimation phase. It may be noted that a decrease in the sublimation intensity due to an increase in the mass concentration of \( \text{Cr(acac)}_3 \) vapors leads to a significant increase in the total desublimation time during induction and sublimation at equilibrium temperature. The effect of heat transfer by radiation, as it turned out, increases with an increase in steam concentration in the medium around the particle. Thus, at vapor concentration of 0.050 and without radiation the particle sublimates in 35 minutes, and with radiation it takes 20 minutes; at vapor concentration of 0.001 without radiation the particle sublimates in 62 minutes, and with radiation – in 38 minutes.

**Figure 3.** Time evolution of the square of the relative particle diameter (a) and the intensity of the precursor vapor entrainment from the particle surface (b) for different temperatures of the sublimator walls.

With a decrease in the sublimator wall temperature and at a constant mass concentration of precursor vapors, the intensity of sublimation as well as the effect of radiation decrease. Figure 3 presents data on the sublimation intensity for the concentration of 0.001 and the temperature range of the medium and the sublimator walls of 190–210 °C. It is worth noting the extreme sensitivity of vaporization of the precursor \( \text{Cr(acac)}_3 \) to a decrease in temperature, which is obviously due to an exponential decrease in the saturation pressure. So reducing the temperature by 20 degrees leads to a threefold decrease in the sublimation intensity and an increase in the time of complete sublimation. At that, the upper temperature limit is bounded by the melting temperature of the particles of 216 °C. A narrow operating temperature range for the sublimators, used in MO CVD technologies, and stringent requirements for maintaining the temperature of all elements of the flow part is a characteristic feature of this coating technology. At the same time, it should be noted that a wide range of organometallic compounds allows choosing the required temperature level, and the choice of particles of a certain fraction, usually 50–1000 microns, allows controlling the intensity and time of complete sublimation, providing the necessary concentration of vapors in the reaction zone.

It is interesting to analyze the characteristic times of induction and sublimation, as well as the effect of radiation on the sublimation of particles of smaller fractions in the conditions closest to practically applicable. Figure 4 presents data on the change in size and intensity of sublimation for particles with diameters of 100, 200 and 300 microns. The calculations were carried out at the maximum permissible temperature in the reactor of 216 °C and a high concentration of precursor vapors close to saturation. It turns out that the induction time for such small particles can reach 1 second, and the total sublimation time is 20 seconds. At the speed (3-6 m/s) of pneumatic transport of particles of this size and weight by gas carrier, the size of the linear (tubular) sublimator would reach 60 meters. It is obvious that sublimation in a swirling flow (gravitational fluidized bed, fluidized bed
in a vortex chamber) is almost a non-alternative method of obtaining precursor vapors with the flow rate necessary for MO CVD process.

![Graph](image)

**Figure 4.** Time evolution of the square of the relative particle diameter (a) and the intensity of the precursor vapour entrainment from the particle surface (b) for different initial particle diameters from 100 to 300 µm.

As can be seen from figure 4b, the intensity of desublimation for such particles during induction significantly exceeds the intensity of sublimation in the future. This suggests that the ingress of a large number of cold particles into the vapor volume in a state close to saturation, will lead to a sharp decrease in the concentration of steam in the mixture and its temperature. When the precursor is dosed, this effect may cause vapor concentration fluctuations in the reaction zone, which may adversely affect the quality of the coating obtained. The data obtained in this paper allow us to approximately estimate the required volume of the steam chamber of the sublimator for a given precursor flow rate.

**Conclusions**

The nonstationary sublimation of spherical particles of \( \text{Cr(acac)}_3 \), floating in the volume of a binary mixture (argon-superheated vapor of precursor) in a reactor with hot walls has been numerically simulated. It is shown that for cold precursor particles entering the sublimation zone in a vortex (or similar) sublimator for MO CVD, there is an induction time during which the particle increases in size, and the vapor concentration and temperature in the sublimator decrease. Even for small particles characteristic of MO CVD technology, the induction time is long if the vapor-gas mixture in the sublimator is close to saturation. It is shown that in the reactor with hot walls, the heat exchange between the particle and the walls of the sublimator due to radiation leads to the particle heating and the intensification of heat and mass transfer. Due to the sensitivity of the sublimation process to temperature, varying the temperature of the walls of the sublimator in a narrow range, it is possible to control the intensity of sublimation of precursor particles. The larger is the particle or the intensity of the mass entrainment removal from its surface, the higher the effect of radiation on the sublimation process is.

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