Influence of radiative heat transfer on the sublimation of a single chromium (III) and zirconium (IV) β-diketonate particle in the argon-helium gas mixture

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Abstract. The paper presents a physical and mathematical model of nonstationary sublimation of single spherical particles of volatile chromium (III) and zirconium (IV) β-diketonates, floating in the flow of a binary argon-helium mixture in a reactor with cold walls. The influence of the carrier gas composition and radiative heat transfer on the kinetics of sublimation has been analyzed. The addition of helium to the carrier gas is shown to increase the intensity of sublimation. The cold walls of reactors decrease the temperature of a particle and increase the time of its sublimation due to the radiative cooling.

1. Introduction
In the aviation and energy industry, there is an urgent need to develop a technology for producing ceramic thermal barrier coatings on gas turbine blades. One of the promising approaches for obtaining thermal barrier coatings is the method of plasma- or laser-activated chemical deposition from gas phase, using volatile compounds of metals with organic ligands (MO CVD) and its varieties for operation at normal and reduced pressure. To implement the method in cost-effective technological processes, it is necessary to provide rather high growth rates of the resulting oxide film with a high completeness of the precursor use. At normal and reduced pressure of the carrier gas, high growth rates can be obtained by increasing the concentration of precursor vapors in the reaction zone (on the heated wall of the blade). High rates of completeness of the precursor use can be achieved by controlling the mixing of the precursor and the oxidizer on the blade wall. One of the ways to solve these problems is the sublimation of the precursor’s particles in the vicinity of the reaction zone under intense heat and mass transfer [1]. As shown in works [2-4], one way to increase heat and mass transfer is to reduce the Prandtl number and Schmidt number by mixing a light gas into the carrier flow (usually argon). Depending on the light component content in the carrier gas, the surface temperature of the sublimating particle may vary. At that the temperature of the particle often increases with a simultaneous increase in the sublimation intensity. An important factor in systems with the precursor phase transition to the vapor phase is the heat transfer by radiation, since in any carrier medium, the temperature of the particles will be lower than that of this medium, and, as a rule,
for high-temperature processes, significantly higher than the temperature of the walls of the sublimation reactor.

In this paper, the physical and mathematical model of nonstationary sublimation of a single particle of a spherical precursor into a mixture of inert gases proposed in [4] is extended to processes with a significant effect of radiation. The article contains results of the model verification on the experimental data on sublimation of chromium tris-acetylacetonate and application of the model to calculate the sublimation intensity for the particles of chromium (III) and zirconium (IV) β-diketonates in a mixture of argon and helium in the reactor with cold walls.

2. Problem formulation and mathematical model

The considered phenomenon is nonstationary sublimation of a single spherical particle of the precursor (chromium (III) acetylacetonate Cr(acac)$_3$ or zirconium (IV) dipivaloyl-methane Zr(dpm)$_4$). The sublimation is believed to occur uniformly over the entire surface of the solid particle, and the bulk sublimation inside the pores of the material is not taken into account. The precursor particle does not lose its spherical symmetry over time. The problem statement and main parameters for the cases of convective and diffusion mode of sublimation are shown in figure 1.

At low velocities of streamlining (diffusion mode of sublimation) the processes of heat and mass transfer in the gas phase are described by a system of parabolic partial differential equations of heat conduction and diffusion of the second order [4]. For multicomponent gas mixtures (three or more components) the diffusion flux of the i-th gas in the mixture can be described by Ramshaw model [5], which is used in [4] and in this work.

At high velocities of streamlining (convective mode of sublimation) the heat and mass transfer intensity on the particle surface is determined by the Ranz-Marshall similarity equations [6]:

\[
\text{Nu} = 2 + 0.6 \text{Re}^{0.5} \text{Pr}^{0.3}, \quad \text{Sh} = 2 + 0.6 \text{Re}^{0.5} \text{Sc}^{0.3}.
\]  

The ratio between concentrations of inert components of the mixture is determined from the solution of the sublimation problem at zero streamline velocity of the particle (in the diffusion approximation) [4]. Taking radiation into account, obtain the following formulation of the boundary conditions on the surface of the particles to solve the heat problem:

\[
q_{r_{c}}^s = \Delta h \left( J_{r_{c}}^s \left(1 - K_{r_{c}}^s \right) + e_{r_{c}} C \left(T_{r_{c}}^s - T_{0}^s \right) \right) + \frac{\lambda_{r_{c}}}{d} \left( T_{r_{c}}^s - T_{0}^s \right),
\]

\[
q_{r_{c}}^s = \text{Nu} \left( K_{r_{c}}^s \right) J_{r_{c}}^s = \text{Sh} \left( K_{r_{c}}^s - K_{10}^s \right) \rho_{r_{c}} D_{r_{c}}^s.
\]
where: \( \rho^g \) and \( \lambda^g \) are the density and thermal conductivity of the mixture of precursor vapor and carrier gases, and \( D^g_{Ki} \) is the diffusion coefficient of vapor in the mixture of carrier gases, the composition of which is determined by a preliminary calculation in the diffusion mode:

\[
D^g_{Ki} = \left[ \sum_{i} \frac{K^g_{i}}{M_i} \right] \left[ \sum_{i} \frac{M_i D^g_{Ki}}{M_i} \right],
\]

\( d \) is the particle diameter, \( T^s_{Ki} \) and \( K^s_{Ki} \) are the temperature and concentration of precursor vapor at the phase transition boundary, \( T^i_{Ki} \) and \( K^i_{Ki} \) are the temperature and concentration of precursor vapor in the incoming flow, \( \Delta h \) is the enthalpy of sublimation, \( \varepsilon_{ef} \) and \( C \) are the emissivity and Stefan-Boltzmann constant, \( T^i \) is the initial temperature of particles and the temperature of cold walls of the reactor, and \( \psi^s_{Ki} = \left( \lambda^s \frac{\partial T}{\partial r} \right)_{r=R^s} \) is the heat flux density to the boundary of the phase transition within the particle, which is determined from the solution of the differential equation of transient heat conduction:

\[
c^p \rho^p \frac{\partial T}{\partial \tau} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \lambda^s \frac{\partial T}{\partial r} \right).
\]

Initial and boundary conditions, determining the size of computational domain and testing the solution method for the binary system Cr(acac)/Ar, are described in detail in [3, 7]. The mass fraction of the precursor vapor \( K^s_{Ki} \) at the phase boundary is determined by the temperature of the particle surface and the curve of vapor saturation (sublimation curve). According to [8] for chromium (III) acetylacetone, the sublimation curve is described by the formula:

\[
\ln p = 39.197 - 15308.5/T.
\]

For zirconium (IV) dipivaloylmethane the data of work [9], supplemented by results of research specially conducted at IIC SB RAS for a wider range of temperatures, are approximated by the formula:

\[
\lg p [\text{torr}] = 9.89 - 5010/T \text{ for } T < 426 K, \quad \lg p [\text{torr}] = 9.599 - 4847.93/T \text{ for } 426 K < T < 454 K, \text{ and }
\]

\[
\lg p [\text{torr}] = 9.45 - 4780/T \text{ for } T > 454 K.
\]

Enthalpy of sublimation for Cr(acac)\(_3\) is determined according to works [8, 10] as the average value in the temperature range from 340 to 457 K equal to 342.66 kJ/kg. For Zr(dpm)\(_3\), the data for the enthalpy of sublimation, available in the literature, have a large scatter and show a significant temperature dependence. In this paper, the dependence \( \Delta h [\text{kJ/kg}] = 177.6 - 0.2266T \) is chosen for calculations. Important parameters of the problem are the coefficients of binary diffusion of the components of the vapor-gas mixture. The data of [10] were used to determine the diffusion coefficient of Cr(acac)\(_3\) in He: \( D_{Cr(acac)\_3-He} [\text{sm}^2/\text{s}] = 0.0658 (T/273)^{1.75} \) and in Ar [11]: \( D_{Cr(acac)\_3-Ar} [\text{sm}^2/\text{s}] = 0.0678 (T/298)^{1.75} \). For Zr(dpm)\(_3\), there are no data on the diffusion coefficient in the literature. These data were determined by the methods of molecular gas dynamics used for evaluation of the relative change of the diffusion coefficient at the substitution of Cr(acac)\(_3\) by Zr(dpm)\(_3\). It was found that the diffusion coefficient for Zr (dpm)\(_3\) should be 2...4 times lower compared to Cr(acac)\(_3\). In further calculations it was accepted that \( D_{Zr(dpm)\_3-He} = D_{Cr(acac)\_3-He} / 4 \) and \( D_{Zr(dpm)\_3-Ar} = D_{Cr(acac)\_3-Ar} / 4 \). The diffusion coefficient of Ar in He was taken to be \( D_{Ar-He} [\text{sm}^2/\text{s}] = 0.635 (T/273)^{1.552} \exp(-1.71/T) \) [12]. The emissivity was determined by thermal imaging studies: for Cr(acac)\(_3\) it was 0.77, and for Zr(dpm)\(_3\) — 0.65.

3. Method of solution

The main feature of the solution method is integration of the written system of differential equations in moving coordinates \((\tau, \eta)\), where \( \tau \) is the time, \( \eta \) is the relative radial coordinate for the area of gas-vapor mixture \( \eta = (r - R_c)/(R_p - R_c) \) and the area of a solid particle \( \eta = r/R_p \). The position of the
phase change boundary $R_c$ is determined by the sublimation intensity and is time-dependent. Explicit boundary detection allows minimizing the time of computation and improving the accuracy of the results.

4. Model validation on experimental data for Cr(acac)$_3$/Ar system

Figure 2 shows the top-down sequences of video frames, obtained by visualizing the process of sublimation of Cr(acac)$_3$ into the flow of Ar. The velocity of the incoming argon flow was 1.9 m/s. During Cr(acac)$_3$ sublimation the temperature of the oncoming stream was maintained equal to 210±2 ºС. It can be noted that the molded particles are somewhat flattened as the substance is carried away, but they do not lose symmetry with respect to the vertical axis, which gives grounds for applying the simplified model in numerical analysis. The thermograms of sublimation of a molded particle and a crystal of the same initial mass practically do not differ from each other.

![Figure 2](image_url)

**Figure 2.** Visualization of Cr(acac)$_3$ precursors sublimation into the Ar flow vs time from 0 to 10 min.

Figure 3 shows a thermogram of the Cr(acac)$_3$ particle sublimation into argon. The data are presented in comparison with the results of numerical simulation. The results of numerical simulation are in good agreement with the experiment. It should be noted that to describe the level of equilibrium temperature and its growth in the end of the process one should take into account the radiation in the heat transfer model. Although the contribution of radiation to the thermal balance at the phase transition boundary is not large (about 20%), the decrease in the equilibrium temperature of the particle leads to a significant decrease in the saturation pressure of the precursor vapor and consequently to a decrease in the sublimation intensity. Calculations show that the total sublimation time, obtained without taking radiation into account, is approximately half of the time of sublimation, obtained considering radiation.

![Figure 3](image_url)

**Figure 3.** The temperature (scale on the left) and the diameter of the sample (scale on the right) of Cr(acac)$_3$ change in time upon sublimation into the Ar flow: solid lines – calculation without radiation; dotted lines – taking into account radiation; points – experimental data.
5. Results and discussion

Figure 4 presents data on the intensity of sublimation of Cr(acac)$_3$ and Zr(dpm)$_4$ in argon-helium mixture at changes in the carrier medium composition without regard to and with account of radiation at the temperature of the carrier medium of 250 °C and temperature of reactor walls of 25 °C. Figure 5 shows temperature of the particles for the same conditions. It can be noted that regardless of the precursor type, the decrease in the sublimation intensity due to an increase in the argon concentration in the carrier medium leads to an increase in the effect of radiation on the particle temperature and a significant increase in the total sublimation time. So when sublimating zirconium β-diketonates into argon without radiation, the particle sublimes for 1.5 minutes, and taking into account the radiation – for almost 10 minutes. When sublimating into helium (with high intensity), the heat transfer by radiation with the reactor walls practically does not change the temperature of the particles, and the time of total sublimation increases slightly.

![Figure 4](image1.png)

**Figure 4.** The sublimation intensity of Cr(acac)$_3$ (a) and Zr(dpm)$_4$ (b) into the argon-helium mixture ($t_e = 250$ and 320 °C, correspondingly) flowing in the reactor with temperature of the walls 25 °C.

![Figure 5](image2.png)

**Figure 5.** The temperature of Cr(acac)$_3$ (a) and Zr(dpm)$_4$ (b) samples change in time upon sublimation into the argon-helium mixture ($t_e = 250$ and 320 °C, corresp.) flowing in the reactor with wall temperature of 25 °C.

With increasing temperature of the carrier medium, the heat loss due to radiation from the particle surface increases. Figure 4 and 5 present data for the particle streamline velocity of 2 m/s, however the studies have been carried out for a wider range of velocities from 0.5 to 10 m/s. It may be noted that
the effect of radiation increases with a decrease in the particle streamline velocity, which is equivalent to a decrease in the convective heat flux to the surface at the same level of heat loss due to radiation. In general it may be stated that for the investigated range of parameters of Cr(acac)$_3$ and Zr(dpm)$_4$ sublimation into argon-helium mixture, which are acceptable for the construction of high-performance sublimators in MO CVD process of applying thermal barrier coatings using these precursors, heat transfer by radiation is an important component of the process and it must be taken into account in the design of appropriate chemical equipment.

**Conclusion**

The influence of heat transfer by radiation on the sublimation intensity and temperature of Cr(acac)$_3$ and Zr(dpm)$_4$ particles, streamlined by the flow of argon and helium mixture of different composition, has been analyzed. It is shown that for the investigated range of sublimation parameters (flow temperature from 250 to 320 °C and velocity from 0.5 to 10 m/s) in the reactor with cold walls, heat transfer by radiation is an important component of the process, which has to be taken into account when designing high-performance sublimation reactors. The increase in the concentration of helium leads to the intensification of convective heat supply to the surface of the particles, which at other identical conditions reduces the impact of heat loss due to radiation, increases the intensity of sublimation and reduces the time of complete sublimation of the particles. The use of helium or mixtures with its high content is a promising method to improve the efficiency of sublimation reactors.

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