Investigation of heat and mass transfer in sublimation of solid particles

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Abstract. The paper presents the results of an experimental study of heat and mass transfer during the sublimation of single spherical particles of metal-organic compounds in an inert gas flow. A technique for manufacturing samples of a binary mixture of Y(dpm)3 and Zr(dpm)4 is shown. As a result of the research, it was found that heat transfer does not depend on the method of sample preparation, but the front of sublimation becomes three-dimensional much faster for the samples prepared without solvent. It should be noted that after reaching thermal equilibrium, the size of the sample stabilizes and subsequently changes only slightly.

1. Introduction

The process of sublimation is widely used in industrial practice for purification of substances, drying materials, separation of mixtures, coating, air conditioning [1-3]. To understand and improve the existing technological processes, as well as to create new ones, a clear understanding of the mechanisms of transfer processes that underlie them is necessary. However, in the literature there are often significant inaccuracies in the description of such mechanisms [4, 5]. Depending on the required results, chemical-technological processes are most often carried out in either diffusion or convective modes. Thus, there is a need to determine the conditions of their hydrodynamic resistance, and the mass transfer rate in a given mode. Despite the large number of experimental and theoretical studies on heat convection, they are limited mainly to the studies of stability and structure of stationary convective flows [6–9]. Similar data for mass transfer are limited, and a small number of papers [10] are devoted to the study of the development of nonstationary convective regimes. At present, there are no theoretical dependences in the literature that allow one to determine the stability limits of diffusion transfer in the processes of sublimation of pure substances, and especially mixtures.

In most mass transfer processes, two or more phases are involved, in which the concentrations of the target component at equilibrium differ. When two phases interact, in accordance with the second law of thermodynamics, their state changes in the direction of achieving equilibrium, which is characterized by equality of temperatures and phase pressures, and is achieved with equal chemical potentials of each component in coexisting phases [11]. When calculating mass transfer rates, it is necessary to know the equilibrium composition of the phases.

Currently, the class of volatile metal β-diketonates is used in the processes of deposition of single and multicomponent coatings by chemical vapor deposition (MO CVD – Metal-Organic Chemical Vapor Deposition). The technology of chemical vapor deposition is used in the microelectronic and optical industries, in the production of high-temperature crucibles, catalysts, etc. The main advantage of MO CVD technology is its universality, since it covers almost any composition of films. Also the
possibility of applying one- and two-sided films, uniform in composition and thickness, on parts with complex configuration and large area can be attributed to the advantages of this method of deposition. MO CVD technology allows continuous film spraying and can achieve high deposition rates while maintaining high film quality.

Despite the increased interest in volatile metal ß-diketonates, as precursors in CVD processes, a clearly insufficient amount of data relating to the mass transfer of both individual compounds and their mixtures in an inert gas flow should be noted [1-3, 6-8].

From the above, it is possible to single out the main difficulties arising in the study of sublimation processes: mathematical models have a large number of assumptions [2], low thermal stability of compounds [5], insufficient thermophysical data of the precursors [10]. Therefore, there is a need for experimental data on heat and mass transfer processes that occur during sublimation. This paper presents the results of experimental studies of the sublimation kinetics of a single spherical particle of Zr(dpm)₄/Y(dpm)₃ mixtures in a stream of argon.

2. Experimental setup

Figure 1 shows the experimental setup. The main element of setup is a heating channel with a nozzle device (2). The channel is filled with quartz balls to create a uniform flow at the outlet of the confuser. The entire system of gas flow preparation is placed inside a thermostatted case (1). The inert gas (argon) in the channel is heated by applying electric current to the heating element (4) with the power unit of the triac key SB50M3, which is switched on by the thermostat Thermodat 13K6 according to the PID control law. The required temperature level of the flow is set by the user and controlled by a thermocouple installed inside the channel. During the experiment, the temperature of the flow is maintained constant within one degree.

The temperature data acquisition system includes a flow thermocouple installed at the nozzle outlet and a thermocouple of the sample under investigation (7). Signals from microthermopairs of type K are fed through a multichannel amplifier into an ADC, and then go to a data processing program on a PC.

The flow rate of the feed gas (a) is controlled by the digital gas regulator MKS 1179A and the microprocessor-based power supply unit PR4000B. The flow velocity varies within U₀ = 1 ... 2 [m/s]. To study the heat and mass transfer during the sublimation of metal-organic compounds, a number of samples are made from the fine powder of precursors Y(dpm)₃ and Zr(dpm)₄. The samples are moulded spheres with a diameter of d₀ = 4 mm with a microthermocouple located in the centre of the sphere. Sample (7) with an initial room temperature is placed in an argon flow at atmospheric pressure in the range of gas temperatures Tg from 200 to 240 ºС. Using the coordinate device, the test sample is placed on the axis of the gas jet at a distance of one nozzle diameter (12 mm). Fixing the change in the size and shape of precursor samples in the sublimation process is carried out using a Nikon D5300 digital camera with a macro lens (8). During the experiment, the camera operates in automatic mode at specified intervals of shooting time. The registration of the size is synchronized with the measurement of the temperature of the oncoming flow and the spherical sample.

Mixtures of precursors with a molar ratio of ZrL₄/YL₃ components equal to 1:1 were prepared in two ways: (1) by mechanical mixing by thorough abrasion of the respective individual molar ratios of individual compounds in a mortar and (2) by dissolving the necessary suspensions in diethyl ether and subsequent evaporation of the solvent in air [3, 6-8].
3. Sample preparation technique

To assess the change in sample size during sublimation, their shape was assumed to be spherical. To implement such geometry, two methods for the production of samples were developed.

First method involves the use of a solvent (since organometallic powders are not plastic), with which it is possible to “glue” the test compounds. Fine crystals (20–50 µm) of the binary mixture Zr(dpm)₄/Y(dpm)₃ are used as the initial mixture. Moistened with solvent, the starting material is placed on a fluoroplastic film in a metal form consisting of two hemispheres. This method of sample formation involves the reinforcement of the substance with fiberglass to impart stability during sublimation (figure 2). At the same time, the junction of microthermocouples of type K with a wire diameter of 100 µm was placed inside the sample in order to monitor the temperature dynamics.

After complete drying of the solvent, the sample acquires the necessary spherical shape and is ready for use (figure 3). The second method of sample preparation excludes the use of chemical additions (without solvent), the formation occurs only due to heating the crystals of the binary mixture Zr(dpm)₄/Y(dpm)₃ to a certain temperature for a short time, while the subsequent part of the method of obtaining material for research sublimation is preserved (spherical shape, reinforcement, thermocouple inside the sample).
4. Results and discussion

Differences in volatility of organometallic compounds play an important role in interdependence of their rates. The most volatile component of the mixture sublimates faster. Therefore, it is necessary to investigate the kinetics of heat and mass transfer during convective sublimation of binary mixtures of organometallic compounds Zr(dpm)4/Y(dpm)3 into an inert gas flow, taking into account differences in the method of sample preparation.

Figure 4 shows the dependence of the equilibrium sublimation temperature of the sample on the temperature of the gas stream for two methods of preparation of the material. The flow velocity was the same for all experiments and was U0 = 1.3 m/s. Due to the research, it was found that heat transfer does not depend on the method of sample preparation.

![Figure 4](image)

**Figure 4.** The dependence of the equilibrium temperature of sublimation of the sample from the temperature of the gas stream.

Figure 5 shows that when thermal equilibrium is reached, the sample size stabilizes and subsequently changes only slightly.
In the study of samples prepared without solvent, it was found that the front of sublimation becomes three-dimensional much faster. Figure 6 presents data on the dynamics of sublimation and a snapshot of the sample after completion of the experiment.

When visualizing the process, it was found that for particles prepared by method II (without using a solvent) no melting of the sample was observed. A photo of a sample prepared using a solvent can be seen in Figure 2.

As can be seen from the above data, the sublimation of the metal-organic mixture can occur on a developed porous surface. Further studies of the volatility of components and changes in the composition of the vapor during sublimation are needed.

**Figure 5.** Comparison of two sample preparation methods.

**Figure 6.** Dynamics of the diameter of a precursor particle upon sublimation into argon flow Ar.
Conclusion
Based on this study, the methods for experimental investigation of non-stationary processes of sublimation have been developed. New methods for manufacturing samples from the fine powder of precursors Y(dpm)$_3$ and Zr(dpm)$_4$ were obtained. Experiments on the sublimation of single spherical particles of a mixture of organometallic compounds Y(dpm)$_3$ and Zr(dpm)$_4$, prepared in two ways, in an inert gas flow were carried out.

It is established that heat transfer does not depend on the method of sample preparation. It is found that the front of sublimation becomes three-dimensional much faster for the samples prepared without solvent. It is shown that after reaching thermal equilibrium, the sample size stabilizes and subsequently changes only slightly.

Acknowledgments
The work was partially supported by the RFBR according to the research project No. 18-38-00426.

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