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Experiment and modeling of mass-transfer processes of volatile metal beta-diketonates. II. Study of mass-transfer process of tris-(acetylacetonato) iridium(III)

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Abstract

Mass transfer process in tris-(acetylacetonato) iridium(III), Ir(acac)$_3$, is investigated using a special installation with non-stop weighing at atmospheric pressure. Mass transfer rates for this compound are measured under various experimental conditions (within temperature range 186–242 °C, at carrier gas flow rate from 1 to 40 $l \cdot h^{-1}$) for powder and single crystal samples. The effect of purification and storage method on mass transfer rate is stated for this compound. Mathematical models describing sublimation processes are proposed. Comparison with earlier obtained results for tris-(acetylacetonato) chromium(III), Cr(acac)$_3$, is carried out.

Keywords: Tris-(acetylacetonato) iridium(III); Mass transfer rate; Sublimation process; Non-stop weighing; Heat-mass exchange theory

1. Introduction

Recently, titanium electrodes coated with a protective layer of precious metals are increasingly widely used in different branches of industry (electrochemical synthesis, chlorine alkyl industry, etc). One of the most promising methods for obtaining this type of coatings is CVD (Chemical Vapor Deposition) [1,2]. A characteristic feature of CVD of precious metals is the insufficient thermal stability of the initial compound, which puts forward additional requirements to the performance of the deposition process. In our opinion, very promising coatings are those made of metal iridium possessing increased stability to corrosion. Therefore, titanium electrodes coated with iridium seem to be promising for use in various areas of science and technology connected with electrochemical processes. The initial compound which is most often used in deposition is tris-(acetylacetonato) iridium(III), which is explained by its physicochemical properties and thermal characteristics [3–5]. However, a series of difficulties arise in the deposition of metal iridium coatings on large surfaces, due to the kinetic and thermal features of the mass transfer process of the initial compound under the conditions providing high concentration of the initial substance. As it was stated earlier [6,7], in order to develop a "hot" source based on solid precursors, it is necessary to obtain the quantitative data on the kinetics of vaporization of the initial compound, depending on changes of the experimental conditions, and to establish correlation dependencies between thermodynamic parameters and the parameters of mass transfer of the precursor.

Earlier we investigated mass transfer of acetylacetonato chromium(III) [6,7]. On the basis of the obtained experimental results, we proposed mathematical models for the sublimation/vaporization of this compound. It was concluded that the major factors affecting mass transfer process were temperature, carrier gas flow rate, and surface of evaporation. The present investigation continues this type of studies with tris-(acetylacetonato) iridium(III), as the subject of investigation.

The goal of the present investigation is to study Ir(acac)$_3$ mass transfer rate as a function of time at: changes of sublimation temperature; changes of the carrier gas flow rate; changes of the effective surface of the substance evaporation (powder, crystals); changes of purification and storage methods (recrystallization, sublimation), and to develop mathematical models for mass transfer process.

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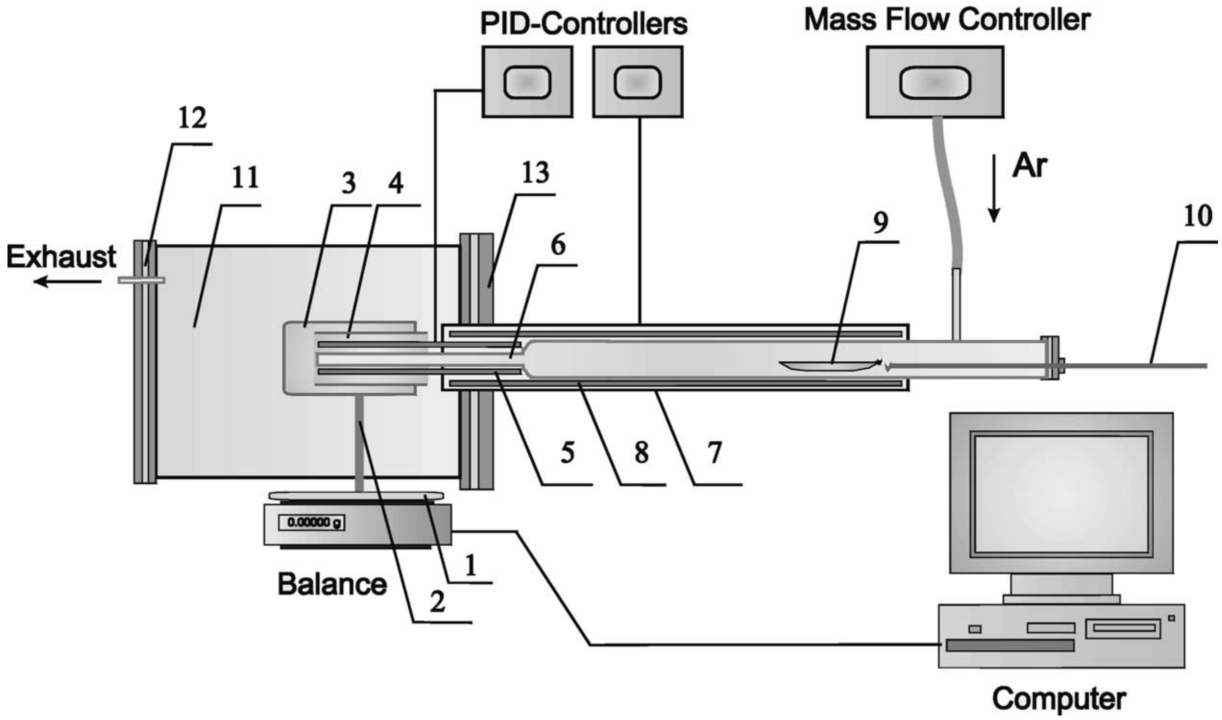

Fig. 1. Installation for study of kinetic of mass transfer processes: (1) plate of electronic balance; (2) holder of condenser; (3) quartz glass; (4) quartz tube; (5), (8) resistive heaters; (6) quartz pipeline; (7) quartz vaporizer; (9) metallic boat; (10) manipulator; (11) quartz reactor; (12), (13) flanges.

2. Experimental

2.1. Synthesis and purification of Ir(acac)$_3$ complex

The initial tris-(acetylacetonato) iridium(III) was obtained according to the procedure developed by us [8] involving the reaction of iridium(III) aqua-complexes with acetylacetone in acidic medium. The product was purified by recrystallization (benzene–hexane system) and double sublimation in vacuum gradient furnace at $P = 5 \times 10^{-2}$ Torr and $t = 170\,^{\circ}\mathrm{C}$. The compound was characterized using its melting point ($t_{\mathrm{melt}} = 265\,^{\circ}\mathrm{C}$) and the data of C, H elemental analysis.

2.2. Characterization of the samples under investigation

Ir(acac)$_3$ *powder.* Powder samples were obtained from the sublimed and recrystallized compound. The sublimed or recrystallized Ir(acac)$_3$ was grained till a uniform powder with particle crystal surface size approximately equal to 0.1–0.2 mm^2 was obtained. Specific surface of the Ir(acac)$_3$ powders was determined by the thermal desorption of argon to be 4.1 m^2·g^{-1}.

Ir(acac)$_3$ *crystals.* The Ir(acac)$_3$ crystals were grown from the solution of this compound in benzene by slow evaporation of the solvent. The time of crystal growth was about two—three months. Flat crystals (1–5 mm high) shaped as hexagonal parallelepipeds with surface area 0.4 to 1.8 cm^2 were obtained.

2.3. Set-up to investigate mass transfer processes

General schematic of the set-up. The mass increase of the condensed substance was determined experimentally using a set-up described earlier in [7]. A scheme of the set-up is shown in Fig. 1.

2.4. Description of the experiment

Evaporator temperature was varied within 186–242 °C. To prevent gaseous compound from condensation at the outlet edge of the heated tube, its temperature was maintained 20–40 °C higher than that in the evaporator. Carrier gas (Ar) was heated preliminarily; its flow rate was varied from 1 to 40 l·h^{-1}. Total amount of the transferred Ir(acac)$_3$ was determined by weighing the condenser before and after the experiment; this amount coincided with the amount of Ir(acac)$_3$ evaporated from the boat. Losses were not more than 5% of the initial weighed portion. The duration of experiments was varied from 90 minutes to several hours, depending on Ir(acac)$_3$ vaporization efficiency.

In order to take account of the influence of temperature and carrier gas flow rate on the operation of the weighing system, a blank measurement without the initial compound before each experiment was made. For this an empty boat was placed into the evaporation region at room temperature; a definite carrier gas flow rate was adjusted. After the balance reached equilibrium, both the heating up process to the experimental temperature and the computer, which captured the measured mass every minute, were switched on simultaneously. The measurements were stopped after 1.5–3 hours.

Table 1
Experimental data for mass transfer of powder $Ir(acac)_3$ samples (sublimation surface area $S = 8$ cm^2)

Charge of $Ir(acac)_3$ [mg]	T [°C]	V_{Ar} [l·h^{-1}]	Number of points	Rate of mass transfer, N [mg·min^{-1}]	N/S [mg·cm^{-2}·min^{-1}]
777	186	2	30	0.15	0.0188
756	210	2	33	0.46	0.0575
669	230	2	40	2.44	0.3050
741	242	2	30	3.80	0.4950
791	220	2	30	1.15	0.1438
667	197	2	30	0.25	0.0313
785	203	2	30	0.37	0.0463
723	203	3	30	0.56	0.0700
664	203	5	40	0.64	0.0800
824	203	7.5	30	0.82	0.1025
910	203	10	30	0.95	0.1188
812	203	15	30	1.06	0.1325
863	203	20	30	1.07	0.1338
879	203	40	37	1.49	0.1863
712	203	1	30	0.18	0.0225

After the set-up was cooled to room temperature, similarly the experiment with the initial substance was carried out under the same conditions. Weighing the condenser and boat before and after experiment was checked by mass balance. The data of the blank measurement and the experiment with the substance were mathematically processed together giving true curves describing the increase of acetylacetonato iridium(III) mass. Total amount of $Ir(acac)_3$, determined using these curves, coincided with the measured amount of condensed $Ir(acac)_3$.

3. Results and discussion

3.1. $Ir(acac)_3$ powder

Weighed portions of the $Ir(acac)_3$ powder (700–1100 mg) were uniformly spread over the surface of the boat, its area being 8 cm^2. The $Ir(acac)_3$ sublimation rate was measured at fixed temperature of the evaporator (186, 197, 203, 210, 220, 230 and 242 °C) at carrier gas flow rate of 2 l·h^{-1}, and at a temperature of 186 °C for the gas flow rates: 1; 3; 5; 7,5; 10; 15; 20 and 40 l·h^{-1}. The lower temperature limit was selected using the data on the temperature dependence of $Ir(acac)_3$ saturated vapour pressure [5] and the sensitivity of the balance. Maximal temperature was limited by the temperature range of sublimation of the initial compound; further increase of the evaporator temperature leads to partial melting of $Ir(acac)_3$ during experiment. The experimental data thus obtained are shown in Table 1.

In order to reveal the effect of the method of purification of the initial $Ir(acac)_3$ on mass transfer rate, the experiments with sublimed compound (1), with the compound purified by recrystallization and kept in air (2), and with the compound recrystallized and dried at 140 °C directly before the experiment (3) were made. The data are shown in Table 2.

Thereby, the purification method and storage history of compound affect the rate of mass transfer. Long storage at the air reduces the rate of mass transfer probably because of water sorption.

Table 2
The $Ir(acac)_3$ mass transfer rate depending on its purification method and storage history ($t = 203$ °C, $V_{Ar} = 2$ l·h^{-1})

Charge [mg]	N [mg·min^{-1}]	Purification method and storage history
1089	0.38	(1)
1010	0.32	(2)
785	0.37	(3)

3.2. Crystals

In order to reveal the influence of effective surface on mass transfer rate, we investigated sublimation of $Ir(acac)_3$ crystals with fixed surface area at $t = 203$ °C, $V_{Ar} = 2$ l·h^{-1}. Crystals with clearly faced surfaces were selected to measure mass transfer rate depending on the surface of sample. Storage conditions for the crystals were the same as those for the sample 2 (Table 2). Surface area of the crystals was calculated using the data on the linear dimensions of the upper surfaces of crystals. One and eight crystals of $Ir(acac)_3$ with the surface areas of 1.62 and 4.86 cm^2 (with approximately equal masses), accordingly, were used. Specific sublimation rates in argon flow were obtained for polydispersed and monocrystal samples to be 0.040 and 0.035 mg·cm^{-2}·min^{-1}, respectively.

We demonstrated earlier [7] that the factor determining integral rate of mass transfer of tris-acetylacetonato chromium(III) is the area of the boundary surface separating gas and the solid sample. In the present investigation we confirmed this conclusion experimentally in the studies of mass transfer of polydispersed and monocrystal $Ir(acac)_3$ samples in inert gas flow.

3.3. Modeling of the sublimation processes of tris-acetylacetonate iridium(III) $Ir(acac)_3$ molecular crystals

As it was stated earlier [6], evaporation/sublimation processes are intensively investigated and described by means of heat and mass transfer theory. This is due to the fact that the use of simplified models for evaporation/sublimation processes without including quantitative characteristics of experimental reactors, like the Hertz–Knudsen–Langmuir model, gives substantially over-estimated process rates, which sometimes differ from the experimental data by 2–3 orders of magnitude. Accordingly, criterial mass transfer models are used recently to describe sublimation processes. These models consider of the experimental features (the geometry of the reactor, dynamics of gas flows, physicochemical characteristics of the substance, etc). Having determined mass transfer coefficient for a process in which a substance with known thermal physical characteristics participates, and knowing the reactor geometry, one can estimate this coefficient for other substances and other experimental conditions using the relations of the similarity theory. This means that the diffusion mass transport can be estimated rather reliably for specific processes and conditions. Such an approach, based on heat and mass transfer theory, turned out to be rather fruitful in the case of metal beta-diketonates; it has been applied in [9–12].

In [6,7] we performed modeling of the sublimation of tris-acetylacetonato chromium(III) and described criterial dependencies for mass transfer processes in argon flow. The flow equation of compound for evaporation or sublimation at proceeding a process in the mode of irreversible is expressed as follows:

$$J = \beta \frac{P}{RT} x_1^0 \tag{1}$$

where J is the flux of the sublimed substance; β is mass transfer coefficient; P is total pressure; R is the universal gas constant; T is sublimation surface temperature, x_1^0 is molar fraction of the diffusing component on the sublimation surface.

On the one hand, this equation indicates a proportional dependence of mass flux on the partial pressure of the evaporating substance; on the other hand, the equation contains mass transfer coefficient β, which can be calculated analytically in some cases; in other cases it may be determined experimentally.

The coefficient β is usually expressed as follows:

$$\beta = \frac{Sh\,D}{d} \tag{2}$$

where *Sh* is the Sherwood's number, D is the diffusion coefficient of the substance under investigation in inert gas flow, d is characteristic length. In the general case, the Sherwood number is a function of the Reynolds' (*Re*) and Schmidt's (*Sc*) numbers:

$$Sh = f(Re, Sc) \tag{3}$$

The following expression is a frequently used version of this functional dependence:

$$Sh = A\,Re^m Sc^n \tag{4}$$

where $Re = \rho V d/\mu$, $Sc = \mu/(D\rho)$, V is linear velocity of carrier gas in reactor section, ρ and μ are the density and dynamic viscosity of the gas phase, respectively (argon in the case under consideration), d is characteristic length of the system, D is diffusion coefficient, A is a constant.

The Schmidt's number is close to unity for gaseous systems, so we used a simplified equation in [6,7]: $Sh = A\,Re^m$. When analyzing the criterial dependencies for the description of mass fluxes of tris-(acetylacetonato) chromium(III), the coefficient m in the functional dependence of the Sherwood's number on the Reynolds' number was found to be 0.43. In Eq. (1), the $\frac{P}{RT}x_1^0$ term is concentration of the sublimed substance at the sublimation surface. We calculated saturated vapour pressure for the compound under investigation using the classical equation: $P = P_o \exp(-\Delta H/RT)$, where ΔH is heat of sublimation of the compound. We used a known equation for the temperature dependence of diffusion coefficient: $D = D_o(T/298)^{1.75}$, where D_o is diffusion coefficient at atmospheric pressure and 25 °C. The effect of temperature on the flow rate of carrier gas was taken into account in a similar manner: $W = W_o(T/298)$, where W_o is the volumetric flow rate of carier gas under normal conditions.

It is known that in the case of laminar flow, for the internal task, the law of the mass transfer is strongly dependent on the length of the tubular reactor [13]. The formation of velocity profile occurs at the initial part of the reactor; then the concentration profile is formed. In case of a long tube, the diffusion Nusselt number (or Sherwood number *Sh*) for the laminar flow aspires to a constant value $Nu_0 = 3.659$, analytically calculated by Nusselt [13].

For the laminar flow, which is steady from the hydrodynamic viewpoint but not steady yet from the diffusion point of view, the analytical solution was obtained by Levec. According to Levec's law, the inter-dependence of the similarity criteria looks like

$$Sh = 1.615 \cdot \sqrt[3]{Re}\,Sc\frac{d}{L}$$

where d is diameter of the tubular reactor, L is its length, *Sc* is Schmidt's number. (The $Re \cdot Sc$ term is often considered as a new similarity criterion *Pe*, Peclet mumber.) One can assume at an accuracy admitted for practical purposes that the Levec law is true at $Pe\frac{d}{L} > 50$, while the law of the steady flow is true when this parameter is less than one [13]. For the experimental reactor, used in the present investigation, we observe an intermediate range in which only empirical formulas can be used.

When analyzing the experimental data on the sublimation of $Ir(acac)_3$, we used the terms of heat and mass transfer theory and the above-written equations. As a result, we obtained the expression for the dependence of *Sh* criterion on *Re* criterion for the sublimation of tris-(acetylacetonato) iridium(III) taking account of different experimental parameters (temperature, inert gas flow rate, sublimation surface, geometry of the sample). This equation is similar to that obtained for the characteristics of tris-(acetylacetonato) chromium(III) sublimation [7] differing only by the factor A. The obtained

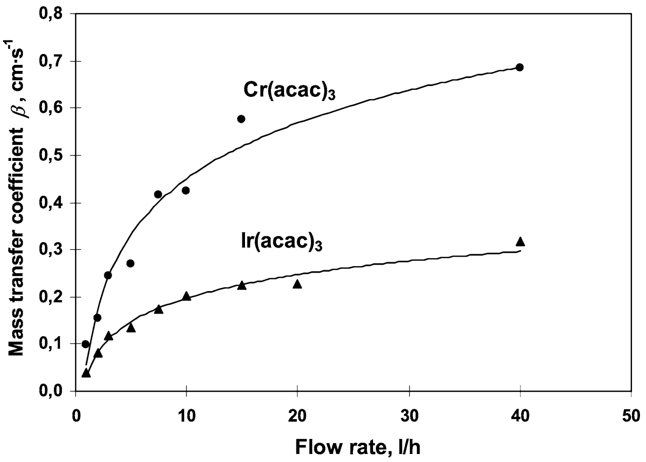

Fig. 2. Dependence of mass transfer coefficient β of sublimation process for acetylacetonates Cr(III) ($t = 197\,^\circ\mathrm{C}$) and Ir(III) ($t = 203\,^\circ\mathrm{C}$) on flow rate of argon.

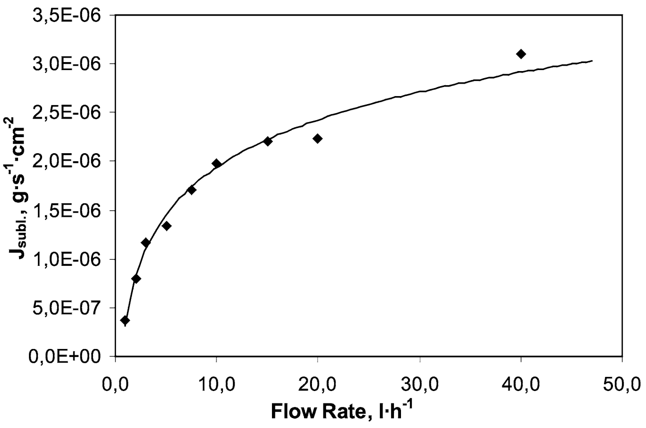

Fig. 3. Dependence of sublimation rate of Ir(acac)$_3$ on flow rate of argon at $t = 203\,^\circ\mathrm{C}$.

expression provides a satisfactory description (with relative error at most 15%) of the influence of experimental parameters on sublimation rate of the molecular crystals of the volatile tris-(acetylacetonato) iridium(III).

Fig. 2 shows dependencies of mass transfer coefficient β on inert gas flow for the samples of acetylacetonato chromium(III) and iridium(III). Evidently, this difference in absolute values of mass exchange coefficients is connected first of all with the decrease of diffusion coefficient (see Eq. (2)) when passing from chromium compound to iridium complex, the latter having larger molecular mass. Using the coefficients of dependence of sublimation rate on experimental conditions, obtained by processing the data for chromium-containing compound, we calculated the theoretical dependence of acetylacetonate iridium sublimation rate on gas flow rate. The experimental and theoretical dependencies are shown in Fig. 3. The deviation of calculated and experimental significances of mass rates of a sublimation does not exceed 15%. Such an agreement between the experiment and calculation can be considered as quite good.

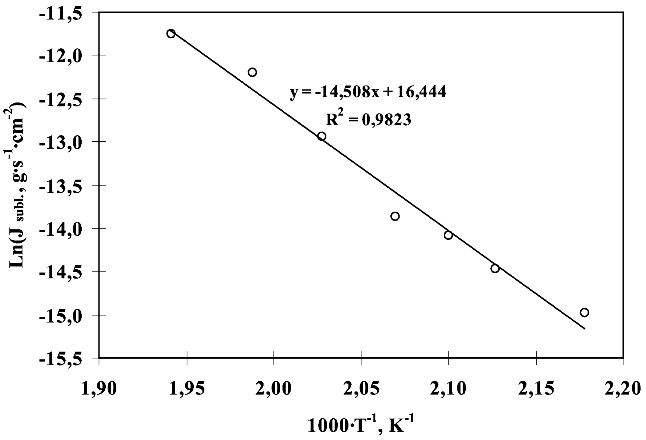

Fig. 4. Arrhenius plot of sublimation rate versus $1/T$ for Ir(acac)$_3$ at $V_{\mathrm{Ar}} = 2\ \mathrm{l{\cdot}h^{-1}}$.

The analysis of the temperature dependence of sublimation rate for identical experimental conditions with respect to other parameters (gas flow rate, sublimation surface, powder sample) allowed us to estimate the activation energy for this process (Fig. 4). The obtained value 120.2 kJ·mole^{-1} agrees with the heat of sublimation for tris-(acetylacetonato) iridium which is 129.2 kJ·mole^{-1} [5]. It should be noted that the whole set of experimental data for chromium- and iridium-containing compounds was processed assuming identical assigned sublimation temperature and the true temperature of sublimation surface. On the other hand, it is well known from numerous experiments on evaporation and sublimation processes that true surface temperature is always lower than the assigned one. This is due to substantial heat removal from surface by the evaporating or sublimating substance. It is this phenomenon that can be responsible for the differences between sublimation heats obtained in the described experiments and the values obtained from tensimetry or similar experiments.

4. Conclusion

Thus, the performed analysis of experimental data on the sublimation of tris-(acetylacetonato) iridium under different experimental conditions confirmed the possibility to develop mathematical models based on heat and mass transfer theory. The obtained empirical dependencies allow one to take account of the effect of experimental parameters and physicochemical characteristics of the substance under investigation on sublimation rate. The model composed using the criterial dependencies not only describes the specific experiment but also provides possibilities to predict the character of the process for other experimental conditions.

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