Chemical deposition process for coatings: 
the problems of mass and heat transfer

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Abstract. The known variants of deposition of thermal barrier coatings (TPC) of ZrO₂-Y₂O₃ by the MO CVD method are analyzed. It is established that the use of this method in principle allows obtaining ceramic coatings with the required columnar structure, low thermal conductivity and technologically acceptable growth rates. It is shown that the main limiting factor in the coating growth rate is the productivity of the precursor vapor sources used. The analysis of known variants of realization of heat and mass transfer at the use of various precursors with a wide range of thermal parameters for the given process is carried out. The results of experimental studies and numerical modeling of the kinetics of sublimation of a number of precursors in the flow of an inert gas Ar, He or their mixtures in a given range of temperatures and gas flow rates are obtained. It is established that when sublimating a single precursor particle under forced convection, the mass transfer intensity of a given compound in the helium stream is several times greater than mass exchange in argon with other closely related parameters, such as the flow velocity and the temperature of the oncoming flow. At the same time, the temperature of the particle is lowered, which can be an important factor in increasing the thermal stability of the vapors. It is shown that there is an additional possibility to control the sublimation of the precursor with the Ar/He mixture.

1. Introduction

At present, many technologies for the deposition of various functional layers using volatile compounds are combined under the common name - chemical deposition of coatings from the gas phase: CVD, MOCVD, ALD, CVI, PECVD and etc [1]. A common ideological platform that unites these processes is the transport of vapors of the initial volatile compound into the deposition zone followed by activated decay on the surface, leading to the formation of a coating. In particular, the processes of chemical deposition from the gas phase using precursors as metal complexes with organic ligands (MOCVD – Metal-Organic Chemical Vapor Deposition) are currently one of the most promising methods of applying a variety of functional coatings [2]. In this case, the layers form during the decay of an "isolated" molecule of a volatile compound on a heated substrate, which allows, by varying the parameters of the experiment, realizing practically any variants starting from a system of unbound nanoparticles up to continuous "thick" micron layers.

MO CVD processes find numerous applications in the production of various types of materials: powders, fibers, thin and thick films, film heterostructures, single crystals, glasses, and their structural
varieties (amorphous materials, polycrystalline materials with various microstructures, etc.) [3]. One of the advantages of the processes under consideration is the possibility of forming compact layers of the highest-temperature oxides and refractory metals (iridium, platinum) at temperatures well below their melting point [4]. To date, from 3 to 5 thousand volatile metal compounds with organic ligands have been synthesized, of which about a fourth have been tested as precursors in MO CVD processes. In the synthesis of precursors, a relatively small number of different organic ligands were used. At the same time, due to changes in the structure of the ligand, the ranges of changes in the physicochemical parameters of precursors and, in the first place, thermal ones, are very wide. So, for example, the molecular weight for typical precursors lies in the range of 100-1500 amu, the van der Waals radius of the molecule is 0.2-1.2 nm, and the vapor pressure at room temperature can vary from dozens to $10^4$ Torr. Thermal stability also varies widely - from room temperature to 700-800 °C. As a rule, in MO CVD processes, when applying a certain type of coating, a large number of different precursors belonging to different classes of chemical compounds can be used [5]. At the same time, depending on the geometry of the product, the way of activating the decomposition reaction, the type, composition, and thickness of the functional layer, the problem of choosing a precursor for the problem posed with an optimal set of thermal parameters arises. The main problems arise in the implementation of long-term and high-speed deposition of layers. In the first case, there is a gradual degradation of the precursor vaporization surface, which can not always be solved by using different types of evaporators. In the second case, the necessary concentration of vapors in the deposition zone and, consequently, the growth rate of the coating can not be achieved due to the fundamental limitations of the thermal parameters of the precursor - an insufficient equilibrium value of the vapor pressure and an appreciable decomposition in the condensed phase at the maximum possible vaporization temperature. The techniques that partially overcome these limitations, for example, solution (aerosol) or melt dosage can be used for a limited type of precursors and some processes [6].

Investigation of the kinetics of vaporization, and in a broader sense, the problems of heat and mass transfer of volatile metal complexes with organic ligands, is extremely sketchy and non-systemic, which complicates the development and implementation of new highly efficient deposition of functional layers by the MO CVD method. Below, this problem will be considered using the example of the formation of an external ceramic layer (COP) of thermal barrier coatings (TBC) for turbine blades by the MO CVD method.

2. Thermal barrier coatings

Ceramic thermobarrier coatings of the hot part of the turbine provide an advantage realized by increasing the temperature limit of the thermodynamic cycle (~ 100..250K) or increasing the life of the turbine blades (up to 2..4 times) [7-10]. Up to now, the main material of COP used to protect the turbine blades using various physical methods are compositions based on ZrO2 and, first of all, ZrO2-7-8% Y2O3 (YSZ). The most widely used are electron-beam devices (EB-PVD) [8] and plasma deposition at atmospheric pressure (Atmospheric Plasma Spraying, APS) [9].

MO CVD processes, with regard to the problems of obtaining TBC, have not been practically investigated. This is surprising, because, for example, the YSZ system is almost a classical object for this method. YSZ coatings were considered as buffer layers for various electronic components, used in high-temperature fuel cells, as sensors and coatings for various functional purposes (optical, biocompatible, hardening). The chemistry of volatile precursors for zirconium and yttrium is quite well developed [5, 11]. There is sufficient voluminous information on the thermal properties of precursors, including the temperature dependence of saturated vapor pressure, thermal stability in the condensed phase, and decay products [12, 13]. The achieved coating growth rates are typical for the classic versions of the MO CVD and do not exceed 2 μm/hr, which is significantly lower than the technologically acceptable rates - from 20 μm/hr [14]. In these processes, the transport of precursor vapor was formed by a vacuum or an inert gas stream over the heated surface of the precursor, which did not provide the necessary concentration in the deposition zone of the coating.
In several papers related to the study of COP TBC deposition processes, the growth rates of YSZ layers of 200-600 μm/h were achieved, which indicates the absence of kinetic limitations for the thermal decomposition reaction used [15-20]. For long processes (3-4 hours), to exclude the heating of the entire mass of the precursor, the dosage of the powder was used in the superheated volume. For shorter time intervals (less than 1 hour), the inert gas was blown over the developed (large area) precursor surface heated to a temperature determined by the thermal stability of the compound in the condensed phase. The share of precursor use did not exceed 25%, which indicates significant shortcomings (low efficiency) of both used precursor vapor transport systems. In almost all of the studies as volatile precursors the dipivaloylmethane derivatives of the corresponding metals, such as tetrakis-2,2,6,6-tetramethyl-heptandionate-2,4-zirconium (Zr(dpm)4) and tris-2,2,6,6-tetramethyl-heptandionate-2,4-yttrium (Y(dpmm)) were used.

3. Studies of heat and mass transfer during the sublimation of a precursor particle under conditions of forced convection

One of the topical tasks in the organization of CVD is the development of effective processes that ensure a high level of mass transfer of precursor vapor into the formation zone of the coating. The results of such experiments are necessary when developing a 'single-source delivery system' for MO CVD reactors. In the literature, a limited number of studies on heat and mass transfer under such conditions are presented [21, 22] and even less studied are transport processes for the sublimation of binary mixtures. Mass transfer in the sublimation of organometallic compounds was considered in [23, 25], in which generalizing correlation dependences were obtained. The relatively low level of the considered temperature range allowed assuming the equality of the temperatures of the ambient space filled with argon and the phase transition surface. In addition, under such conditions, the influence on the heat and mass transfer of the transverse flow of matter can not be taken into account in the construction of correlations.

Various thermodynamic states of matter: stable, metastable and labile in the description of sublimation are discussed in [26]. It is noted, in particular, that in the case of crystallinity sublimation, large grains sublime more slowly than smaller structural formations. If the steam becomes supersaturated, the formation of embryos and desublimation occurs. In desublimation, an important factor at which the desublimation occurs on the surface of the substrate or in the gas phase is the relationship between the intensity of heat and mass transfer [27]. The kinetics of the sublimation process can depend on the value of the Lewis number Le. If Le > 1, the heat transfer will occur more intensively than mass transfer. In this case, the transition to the solid phase will occur not on the wall, but in the flow. Peculiarities of heat and mass transfer during a phase transition arising in binary systems with Le ≠ 1 are considered in [28].

In our work we studied heat and mass transfer in the sublimation of a single particle in an Ar/He...
flow. A sphere with a 4 mm diameter was formed using an organic solvent from of 20-50 μm crystals of Zr(dpm)$_4$ precursors. K type thermocouple was embedded in the center of the junction. The diameter of thermoelectrodes was 100 μm. A sample with an initial room temperature was placed at atmospheric pressure in a gas stream heated to a temperature in the range of 200 to 330°C. During the sublimation, the temperature of the material and changes of its linear size were recorded simultaneously. Details of the procedure are given in [29]. Under the conditions of forced convection, the sublimation kinetics turns out to depend on the nature of the gas. Figure 1 shows that when a Zr(dpm)$_4$ particle flows through a helium stream with a temperature of 277°C, whiskers grow on the surface of the sample. It can be assumed that in the experiment due to the radiation of heat from the stern part of the particle into the surrounding cold space, the surface temperature is locally reduced. This can lead to partial desublimation of the precursor vapor. In [30], when investigating the sublimation of water ice into vacuum, the formation of similar tree-like crystals was recorded. The authors of [30] associated desublimation with the manifestation of a nonequilibrium phase transition (supersaturation of vapors).

The numerical simulation results obtained in this paper for the experimental conditions show a linear decrease in the particle diameter of the particle versus time, and correlate well with the results of the sublimation experiment into the helium flux. As can be seen from figure 2, the sublimation of Zr(dpm)$_4$ to helium occurs much more intensively than to the flow of argon.

We believe that the increase in the intensity of sublimation is primarily due to the greater thermal conductivity and heat capacity of helium than to argon. An increase in these parameters leads to an intensification of heat transfer at the boundary of the phase transition, which leads to an increase in the temperature of the particle and an increase in the vapor pressure at its surface. In addition, at sublimation into helium, the temperature difference between the incoming flow and the equilibrium temperature of the particle during the stabilization stage decreases. This may be important for CVD processes in which thermally unstable organometallic compounds are used.

4. Discussion and Conclusion
It is shown that there is an additional possibility to control the sublimation of the precursor with the Ar/He mixture. Estimates have shown that changing the composition of the gas mixture can affect the intensity of mass transfer and change the level of the partial pressure of the precursor vapor.

As the sublimation temperatures rose to ~ 260°C, close to the triple point, the formation of a "whisker" on the phase transition surface was recorded. The number of whiskers in the helium atmosphere is several times higher than the sublimation in the argon flow. The IR spectroscopy data served to establish the identity of the whiskers composition of the initial precursor composition.

The data obtained on the peculiarities of heat and mass transfer of precursors in a vortex evaporator were used in the development of a high-performance vapor source for the experimental MOCVD reactor for the formation of thermal barrier coatings (TBC) on the turbine blades.
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