

STUDY OF THE PROCESS OF THERMAL DISSOCIATION OF TANTAL PENTACHLORIDE IN VACUUM

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The dependence of the degree of dissociation of $TaCl_5\alpha(T, P)$ vapors on the temperature in the range of 1470...1820 K in a vacuum of $1.33 \cdot 10^{-2}$ Pa was by using of equilibrium chemical thermodynamics obtained. The experimental data on the dependence of $\alpha_{ex}(T, P)$ on temperature and vapor mass flow $TaCl_5$ were analyzed and compared with calculations.

INTRODUCTION

The aim of the work is to study the process of thermal dissociation of tantalum pentachloride vapors in the range of 1470...1820 K in a flow vacuum system, focused on achieving the possibility of obtaining coatings Ta thick $\geq 250 \mu m$ in the form of a sealed corrosion-resistant shell under irradiation with high-energy-electrons in the aquatic environment on tungsten plates of size $66 \times 66 \times 3; 4; 6; 10$ mm, which are neutron-forming elements of the "Source of neutrons" target.

1. EQUILIBRIUM CHEMICAL THERMODYNAMICS THERMAL DISSOCIATIONS $TaCl_5$

The general issues of obtaining solid phase condensates by deposition from the gas phase using the CVD method are described in monographs [1]. A special case of the kinetics of heterogeneous reversible reactions of the type $A \leftrightarrow vB$ was considered in [2]. In the specific case, the deposition of tantalum from the vapors of the pentachloride is carried out in a flow-through vacuum system (in contrast to the Van Arkel-De Boer method, which is implemented in a closed volume).

The use of vacuum conditions during the thermal dissociation of $TaCl_5$ allows the deposition of tantalum coatings at an observable rate. Reduced pressure contributes to an increase in the degree of conversion for reactions that occur with an increase in the number of particles in the gas phase in accordance with the principle of Le Chatelier. It is the use of vacuum that allows the process of thermal dissociation of $TaCl_5$ to produce solid tantalum.

The technological parameters (substrate temperature, pressure near the condensate growth surface, specific mass flow of pentachloride vapors) determine the rate of precipitation (etching) of tantalum, as well as the structure and properties of the coating. Thermodynamic calculations of the equilibrium of the chemical reaction used make it possible to estimate the range of changes in the technological parameters for an efficient process, and the comparison with experimental data optimizes the deposition conditions from the point of view of obtaining coatings with desired properties.

The deposition rate of tantalum is:

$$V_{Ta} = \beta \alpha_{TaCl_5}(P, T) \frac{\Delta m_{TaCl_5}}{\Delta t \rho_{Ta} S} \cdot \frac{A_{Ta}}{M_{TaCl_5}}, \quad (1)$$

β – coefficient depending on the geometry of the reactor (empirically); $\alpha_{TaCl_5}(P, T)$ – equilibrium degree of transformation $TaCl_5$ at a pressure P (atm) and a deposition temperature T ; Δm_{TaCl_5} – the mass of $TaCl_5$, supplied to the surface area of S for the time Δt ; ρ_{Ta} – density Ta; A_{Ta} – atomic weight Ta; M_{TaCl_5} – molecular weight $TaCl_5$.

For reaction



running in equilibrium conditions, the value is determined by the ratio:

$$K_p = 5^5 \alpha^5 P^4 / (1 - \alpha)(1 + 4\alpha), \quad (3)$$

where K_p is the equilibrium constant:

$$K_p = \frac{P_{Cl}^5}{P_{TaCl_5}} \times a_{Ta}, \quad (4)$$

P_{Cl}, P_{TaCl_5} – partial pressures Cl and $TaCl_5$, a_{Ta} – tantalum activity, $a_{Ta} = 1$.

Equilibrium constant K_p is associated with a change in the Gibbs free energy as a result of the reaction of the Gibbs-Helmholtz equation (entropy approximation, $\Delta C_p = 0$):

$$\Delta G_{reaction} = \Delta H_{298}^{reaction} - T \Delta S_{298}^{reaction}, \quad (5)$$

where $\Delta H_{298}^{reaction}$ and $\Delta S_{298}^{reaction}$ – changes in enthalpy and entropy, respectively:

$$\Delta H_{298}^{reaction} = \sum \Delta H_{298}^{\circ}(pr.) - \Delta H_{298}^{\circ}(in.), \quad (6)$$

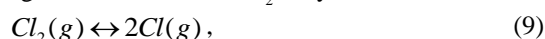
$$\Delta S_{298}^{reaction} = \sum S_{298}^{\circ}(pr.) - S_{298}^{\circ}(in.), \quad (7)$$

ΔH_{298}° – the enthalpy of formation of each of the participating substances (*pr.* – reaction products, *in.* – initial materials) at $T = 298$ K, S_{298}° – entropy, respectively, at $T = 298$ K, and:

$$\Delta G_{reaction} = -RT \ln K_p, \quad (8)$$

R – ideal gas constant $R = 8,32 \frac{J}{K \cdot mol}$

The validity of writing the process equation in the form (2) is confirmed by the calculation of the equilibrium degree of dissociation $Cl_2\alpha$ by the reaction



$$K_p = 4\alpha^2 P / (1 - \alpha^2), \quad (10)$$

and

$$\Delta G_{\text{reaction}} = 242600 - 107.181 \cdot T \text{ (J/mol)}, \quad (11)$$

and reference values for standard enthalpy and entropy are given below.

$$\begin{aligned} \text{TaCl}_5(\text{g}): \Delta H_{f298} &= -182.25 \text{ Kcal/mole [3]} \\ \Delta H_{f298} &= -182.4 \text{ Kcal/mole} = -763672 \text{ J/mol [4]} \\ S_{298} &= 102.6 \text{ cal/mole K} = 429,566 \text{ J/(mol K) [4]} \\ \text{Ta(s)}: S_{298} &= 9.92 \text{ cal/mole} \\ K_p &= 41.533 \text{ J/(mol K) [4]} \\ \text{Cl(g)}: \Delta H_{f298} &= 121302 \text{ J/mol [5]} \\ S_{298} &= 165.076 \text{ J/(mol K) [5]} \\ \text{Cl}_2(\text{g}): S_{298} &= 222.965 \text{ J/(mol K) [5]} \end{aligned}$$

The results of calculations according to equation (10) are given in Fig. 1.

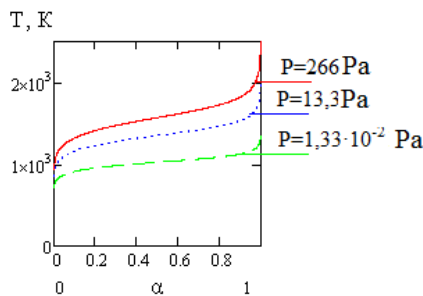


Fig. 1. The ratio between the degree of dissociation diatomic chlorine and temperature

So, in a practically interesting temperature and pressure range, the value α_{Cl_2} is close to unity, which allows reasonably calculating the process equilibrium in accordance with writing the reaction equation in the form (2), the change in the free energy of which, taking into account the above reference data, is:

$$\Delta G_{\text{reaction}} = 1470182 - 437.347 \cdot T \text{ (J/mol)}, \quad (12)$$

Taking into account expressions (3), (8) and (12), we calculate the dependence of temperature on the degree of conversion for pressure $P = 2; 0.1; 10^{-4}$ mm Hg, respectively (Fig. 2)

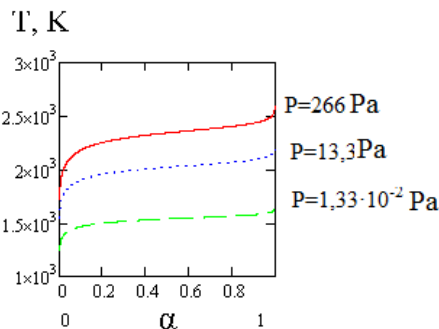


Fig. 2. Dependence of temperature change T, K on the degree of transformation α for reaction (2) at pressure values 266; 13.3; $1.33 \cdot 10^{-2}$ Pa

Fig. 3 shows the dependence of pressure on the degree of transformation α .

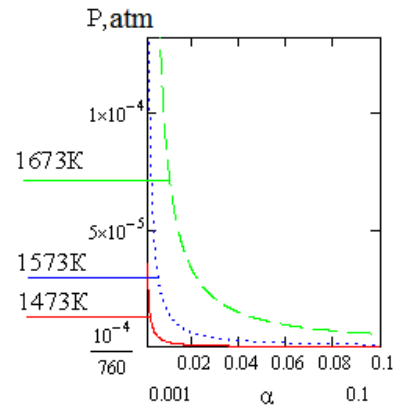


Fig. 3. The dependence of pressure P on the degree of transformation α according to reaction (2) for temperatures of 1473, 1573, and 1673 K

The dependence of temperature on pressure for the values of the degree of transformation $\alpha = 0.1; 0.4$, and 0.7 is presented in Fig. 4.

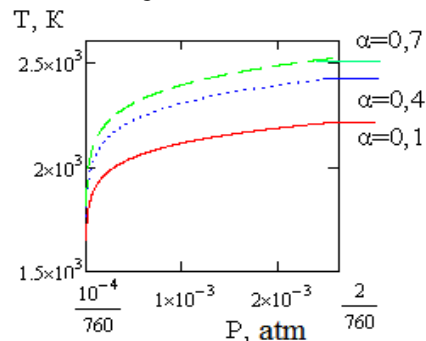


Fig. 4. The dependence of temperature change on pressure for the reaction (2), where the curves are given for the degree of transformation $\alpha = 0.1; 0.4$, and 0.7

The dependence of the vapor pressure of TaCl_5 in the range of $298 - T_{\text{melt}}$ in accordance with equation [6]:

$$\log P = -\frac{6275}{T} + 34.305 - 7.04 \log T \text{ (mm Hg)} \quad (13)$$

graphically presented in Fig. 5.

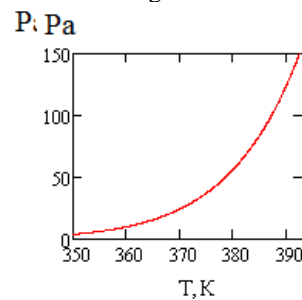


Fig. 5. The dependence of vapor pressure tantalum pentachloride TaCl_5 on temperature

The combination of the above data (Figs. 1–5) makes it possible to evaluate the necessary parameters of the technological process (intervals of deposition and evaporation temperatures of tantalum pentachloride, pressure in a vacuum chamber) before the Ta deposition experiments.

2. EXPERIMENTAL STUDY OF THE TANTALUM DEPOSITION RATE DEPENDENCE ON TEMPERATURE AND MASS FLOW $TaCl_5$

Experiments on the deposition of tantalum were done in a vacuum unit with a residual pressure of atmospheric air of $1.33 \cdot 10^{-2}$ Pa. Samples of tantalum foil with a thickness 0.3 mm and a size of 50×10 mm were used as substrates. This made it possible to exclude the influence of a material other than tantalum on the deposition process, since tantalum pentachloride enters into chemical interaction with practically most materials at a deposition temperature T_a . For heating the samples used a water-cooled inductor made of a copper tube $\varnothing 10 \times 1$ mm as a flat Archimedes spiral turns of 6, the inductor is loaded onto the same axis and that arranged at a distance of ~ 5 mm composite (two discs) graphite disk $\varnothing 100$ mm with a cut-out in the form of a radial sector for placement on a large disc diameter of the sample to be coated tangentially to the circumference of the discs. The edges of the sample were clamped between two disks (4 mm thick each) of graphite to create an electrical contact in order to close the circular currents induced in the disks, and thereby ensure heating of the samples (Fig. 6). The inductor was powered from a high-frequency installation VCHI-63-0.44, operating at a frequency of 440 kHz.

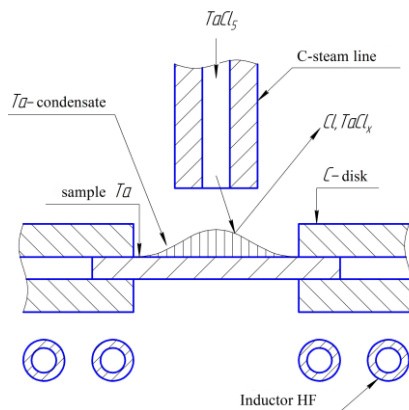


Fig. 6. Scheme of the device for the study of CVD deposition process Ta of $TaCl_5$

A graphite tube-steam line with a hole of $\varnothing 4$ mm at its end for the expiration of tantalum pentachloride vapor entering through the steam line from the removable evaporator was placed at a distance of 5 mm perpendicular to the central part of the sample plane. The evaporator was maintained at a temperature in the range of $360 \dots 390^\circ K$ with an accuracy of $\pm 0.5^\circ K$, set by a contact thermometer such as MKT with an electronic key. The change in the mass flow of tantalum pentachloride vapors to the surface of the substrate and thereby the regulation of the effective pressure in the deposition zone of the coating was achieved by changing the temperature of the evaporator. The amount of pentachloride evaporated during Δt was determined by weighing the evaporator with its shutter closed before and after the experiment on the BTU-2100 scale. In this case, the evaporator was disconnected from the vacuum chamber using a detachable vacuum connection. In the course of the experiment, the temperature of the sample was con-

trolled using an optical pyrometer of the "Promin" type and operated by changing the high-frequency radiation power supplied to the inductor from the VCHI-63-0.44 generator. The amount of tantalum condensate deposited during Δt was determined by weighing the sample before and after the experiment using a VLR-20 type balance. The coating thickness was measured using a micrometer according to the difference of the data before and after deposition, as well as using microsections.

In Fig. 7 presents data on the dependence of the experimental utilization factor of tantalum pentachloride α_{ex} on the substrate temperature, which is proportional to the deposition rate of the coating in equation (1). α_{ex} increases rapidly at temperatures above $1470^\circ K$ until reaching saturation at $\sim 1820^\circ K$.

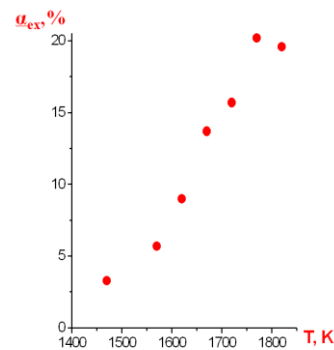


Fig. 7. Experimental dependence the yield of Ta from $TaCl_5$ to the coating from the substrate temperature

The value α_{ex} does not reach the calculated equilibrium value α due to the presence of the coefficient $\beta < 1$ in equation (1), which depends on the geometry of the reactor used and indicates the degree of unproductive scattering of tantalum pentachloride into the vacuum that is not involved in the coating condensation process under equilibrium conditions. The data in Fig. 7 refer to the value of 5 g/h of the mass flow of tantalum pentachloride.

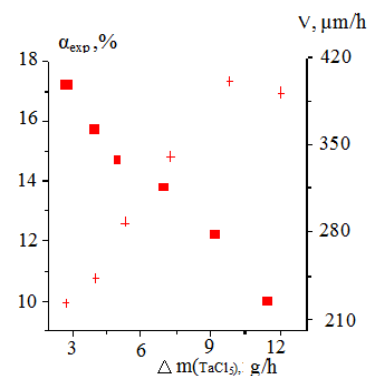


Fig. 8. Experimental dependence of Ta yield from $TaCl_5$ to the coating on the $TaCl_5$ mass flow $TaCl_5$ (■) and the growth rate of the coating on mass flow of vapors of $TaCl_5$ (+). All data obtained at a temperature of $1720 K$

Fig. 8 shows the dependences α_{ex} (■) and the corresponding deposition rate of the coating V (+) in equation (1) on the mass flow of tantalum pentachloride. The

data in Fig. 8 correspond to the process at a substrate temperature of 1720 K.

The yield of α_{ex} of tantalum to the tantalum pentachloride coating decreases from ≈ 17 to $\approx 10\%$ with an increase in the mass flow of pentachloride from ≈ 3 to ≈ 11 g/h. This corresponds to the principle of Le Chatelier, according to which an increase in the effective pressure should suppress the yield by reaction with an increase in the number of particles in the gas phase.

So, an increase in the effective pressure P of tantalum pentachloride near the surface of the substrate, due to an increase in the value $\frac{\Delta m_{\text{TaCl}_5}}{\Delta t}$ in equation (1), leads to a decrease in the equilibrium yield α for the reaction under consideration.

However, as α decreases, the deposition rate V increases (at a given temperature), since the mass flux of tantalum pentachloride, which appears in equation (1) as a linear multiplier, increases.

Practically, when developing a technology for applying tantalum coatings on specific products, the required consumption of pentachloride and the deposition rate of tantalum should be chosen, taking into account the nature of the experimental dependencies shown in Fig. 8a and 8b. This will allow both economical use of expensive tantalum pentachloride and optimize the temperature regime of the process and, accordingly, adjust the finishing properties of coatings, which determine the operational efficiency and service life of coatings.

CONCLUSIONS

1. The influence of the substrate temperature and pressure on the process of thermal dissociation of tanta-

lum pentachloride vapors on the heated surface in the interval of $\sim 1470 \dots 1820$ K was investigated and the calculated thermodynamic equilibrium data were compared in comparison with experimental ones.

2. The rate of deposition of tantalum increases with increasing mass flow of vapor of its pentachloride; at the same time, the utilization rate of tantalum pentachloride decreases, i.e. its unproductive losses are increasing due to vapor scattering inside the vacuum chamber.

Saving costly tantalum pentachloride can be achieved by selecting the optimal process parameters based on the data of this work.

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ИССЛЕДОВАНИЕ ПРОЦЕССА ТЕРМИЧЕСКОЙ ДИССОЦИАЦИИ ПЕНТАХЛОРИДА ТАНТАЛА В ВАКУУМЕ

Ю.И. Поляков, С.Г. Руденький, Ю.В. Лукирский, И.И. Коновалов, В.И. Рак

В рамках равновесной химической термодинамики получена зависимость степени диссоциации паров $\text{TaCl}_5\alpha(T, P)$ от температуры в интервале 1470...1820 К и вакууме $1,33 \cdot 10^{-2}$ Па. Проанализированы и сравниваются расчетные данные с экспериментальными данными зависимости $\alpha_{\text{экс}}(T, P)$ от температуры и массового потока паров TaCl_5 .

ДОСЛІДЖЕННЯ ПРОЦЕСУ ТЕРМІЧНОЇ ДИСОЦІАЦІЇ ПЕНТАХЛОРИДУ ТАНТАЛУ У ВАКУУМІ

Ю.І. Поляков, С.Г. Руденький, Ю.В. Лукирський, І.І. Коновалов, В.І. Рак

У рамках рівноважної хімічної термодинаміки отримана залежність ступеня дисоціації парів $\text{TaCl}_5\alpha(T, P)$ від температури в інтервалі 1470...1820 К і вакуумі $1,33 \cdot 10^{-2}$ Па. Проаналізовано та порівняно з розрахунковими експериментальні дані залежності $\alpha_{\text{експ}}(T, P)$ від температури і масового потоку парів TaCl_5 .