THE ROLE OF GAS-PHASE TRANSPORT IN COMBUSTION OF THE TANTALUM—CARBON SYSTEM

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Gas-phase transport during combustion of powder mixtures attracts more and more attention in self-propagating high-temperature synthesis (HTS) investigation. In application to infusible powder mixtures consisting of particles of different species, it is considered as a process necessary for combustion wave propagation since purely diffusion interaction cannot be assured by the sufficiently high chemical reaction rate because of the small contact surface between reagent particles [1].

The influence of gas-transporters on the HTS process was first described in [2, 3]. Investigation of the influence of active gasifying additions on the combustion regularities of mixtures of molybdenum with boron showed that the oxidizing compounds ($KClO_3$, $NaNO_3$, etc.) substantially intensify the combustion process while the additive-reducers (NH_4Cl, NH_4N_3, etc.) diminish the combustion rate [2]. The influence of the gas impurities (particularly hydrogen) being contained in the initial components, on the rate and completeness of the reaction is demonstrated in investigations of the combustion regularities in the weakly exothermal system TiC—WC [3]. The effect of the gas-phase interaction during combustion of the titanium—carbon system [4] is manifest in a narrow domain of the heating zone and is explained by the interaction of titanium particles with the hot gases being liberated in the high-temperature zone of the combustion wave. An increase in the CO pressure when carrying out the process in a CO atmosphere magnifies the gas-phase interaction effect. The role of silicon gasification during its combustion in nitrogen is analyzed in [5].

Therefore, the gasification of reagents, additions, or impurities influences the combustion mechanism and regularities in different HTS-system classes. This influence appears most graphically in systems whose combustion temperature is below the melting points of the reagents and products since the more intensive factor is missing in this case, the transport of reagents by the spreading melt. The tantalum—carbon system during whose combustion a significant quantity of gases, H_2, CO, and CO_2, is liberated [6] satisfies this condition. Consequently, a study of the gas-phase transport in the system Ta—C without gasifying additions, except due to impurities being contained in the initial reagents, is of scientific and practical interest.

Powders of tantalum primary (MRTU 95-136-69), soot PM-15, and pulverized graphite were utilized to prepare the reaction mixtures. Filaments, wires, and foils of the initial reagents were used for experimental modeling of the reaction cell.

The diagram and results of the first series of experiments are presented in Fig. 1. Cylindrical specimens of 20 mm diameter and 30 mm altitude within which a cavity of 1-2 mm diameter was drilled, were pressed from Ta + C mixtures. Segments of tantalum wire of 50 mm diameter were placed in the cavity such that they did not touch the walls. The inner cavity walls were clad by a tracing paper layer in certain specimens to exclude the random incidence of mixture particles on the wire surface. The HTS reaction $Ta + C \rightarrow TaC$ that was propagated in the form of a combustion wave [4] was induced in the prepared specimen. The process was conducted in an argon medium at pressures to 1 MPa. Study of the wires by using a scanning electron microscope showed that a layer of product of ~2 μm thickness (Fig. 1b) is formed on the tantalum surface. An x-ray microanalysis shows that this layer contains tantalum and carbon and the gold tinge of the layer permits the assumption that it consists of tantalum monocarbide. The thin layers (to 2-3 μm) have the characteristic micromorphology

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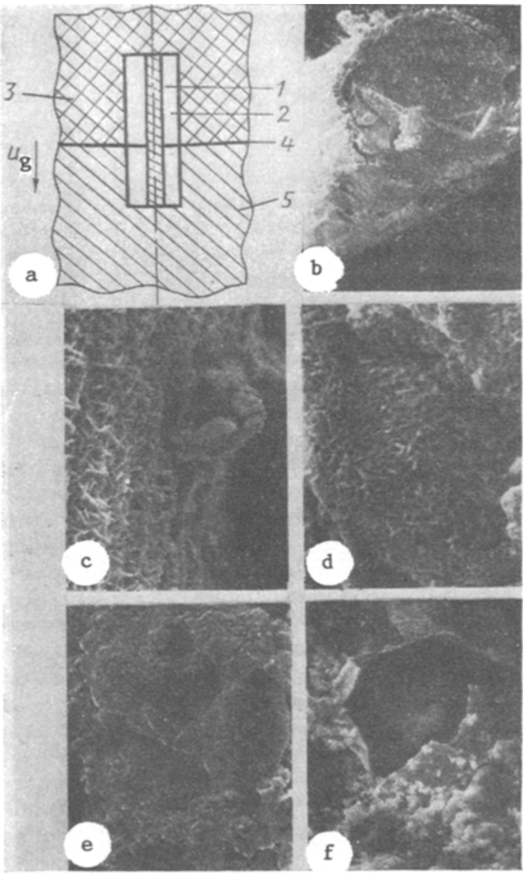

Fig. 1

(Fig. 1c). If the cavity 2 is filled with graphite powder or a mixture of Ta + C, the thickness of the layer being formed on the tantalum wire surface increases to 10-15 μm and the microstructure represented in Fig. 1c is replaced by a globular structure.

When 6-μm-diameter carbon filaments were used instead of wires in these experiments, no carbide layer was formed on them. Only scarce tantalum-containing particles are detected on the carbon surface. The surface itself is here quite broken up.

The results show that gas-phase transport of carbon and its interaction with tantalum are realized under the conditions produced by the combustion wave in the reactive Ta + C medium, whereupon a layer of product is formed. Tantalum transport is realized to a much smaller degree as compared with the carbon transport.

Specimens of the system Ta + C with a quenched combustion front were obtained and investigated in order to compare the results of model experiments with the combustion wave microstructure. Quenching was realized in a wedgelike cutout of the cooling copper module by the method in [7]. Microstructures characteristic for different zones of the HTS quenched wave are represented in Fig. 1d-f. Near the leading boundary of the combustion front, a product layer whose structure (Fig. 1d) is analogous to the structure of the product being formed because of gas-phase transport in the model experiments (Fig. 1c) is formed on the tantalum particle surface. The difference is just in the scales of the structural components: The structure in the quenched specimen is shallower than on the wire surface.

A gradual "rounding off" of the structural components is observed in the higher temperature domain (Fig. 1e); globular formations start to predominate in the product. The

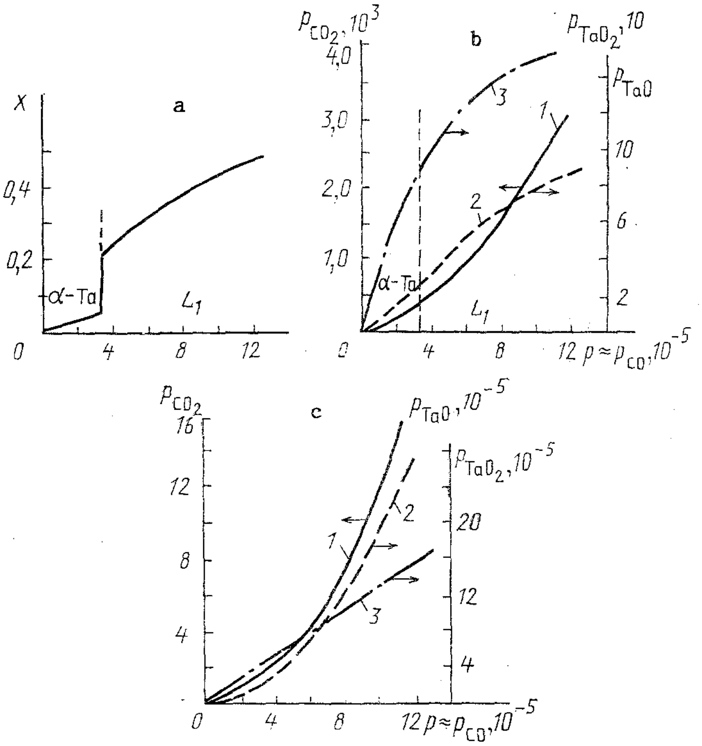

Fig. 2. Equilibrium content of oxygen in tantalum (a) and equilibrium pressure of gases above the tantalum surface (b) and carbon (c) as a function of the CO pressure at the combustion temperature of 2500 C (1 – CO_2 pressure, 2 – TaO_2, 3 – TaO), x, atomic fraction; p, Pa.

final product of the synthesis consists of round TaC particles and also contains a certain quantity of hollow "shells" (Fig. 1f).

Therefore, the product layers with structures characteristic for gas-phase transport are formed not only in the model tests but also in the low-temperature domain of the combustion wave (possibly in the heating zone already). It should be noted that the layer mentioned covers the whole tantalum particle surface while, according to data of electron microscope investigations, direct contact between the tantalum and the carbon particles in the charge exists just at individual points. This also shows that carbon transport to the tantalum surface in the combustion wave can occur through the gas phase.

A thermodynamic estimate of the gas phase composition above the surface of the carbon and tantalum particles (see Appendix) was performed in order to analyze the possible mechanisms of gas-phase transport of carbon. We here started from the assumption, verified by experiment, that carbon gasification occurs principally in the CO form. An oxygen impurity is contained in both the tantalum powder (0.3 mass %) and in the carbon materials (from 0.4 to 2 mass %) used in the tests. It is easy to estimate that the passage of the whole impurity oxygen into the gas phase in the form of CO could be produced in the specimen pores by a pressure of tens of atmospheres. The time of CO desorption from the carbon surface, estimated by using the approach [8] to the coal and graphite gasification reaction in a $CO + CO_2$ atmosphere is $5 \cdot 10^{-4}$ sec at 1600°C and $2 \cdot 10^{-5}$ sec at 2400°C, i.e., is sufficiently small. The results of thermodynamic computations (see Appendix) are represented in Fig. 2. It is seen that the equilibrium pressure of CO_2 above the tantalum surface is approximately three orders of magnitude greater than above the carbon. The partial pressures of TaO and TaO_2 are negligibly small as compared with the CO, CO_2 pressures.

The metal surface layer is saturated by oxygen and carbon [9]

$$CO_{(g)} \rightleftarrows [C]_{Ta} + [O]_{Ta} \qquad (1)$$

for carbon monoxide adsorption by tantalum.

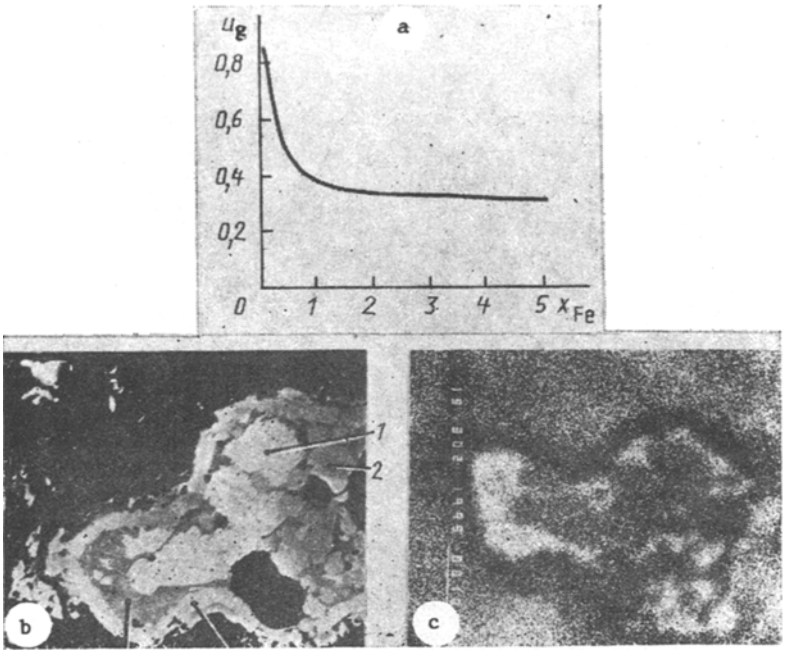

Fig. 3. Dependence of the combustion rate of the composition Ta + C on an iron addition (a) and an underreacting tantalum particle in the system Ta + C (b, c); b) image of a microsection in reflected electrons "compo"; c) the same section in characteristic K_α radiation (1 – Ta; 2 – TaC grain; 3 – metallic "batch"; 4) TaC shell), ×3000.

The carbide TaC is formed in the near-surface tantalum volume

$$[C]_{Ta} + Ta \rightleftarrows TaC_{(s)}, \qquad (2)$$

and the excess oxygen reacts with the CO to form carbon dioxide

$$[O]_{Ta} + CO_{(g)} \rightleftarrows CO_{2\,(g)} \qquad (3)$$

The set of elementary stages (1)-(3) can be represented in the form of the following gross reaction that progresses on the tantalum particle surface

$$Ta + 2CO_{(g)} \rightleftarrows TaC_{(s)} + CO_{2\,(g)} \qquad (4)$$

The equilibrium constant of this reaction $K_e = p_{CO_2}/p_{CO}{}^2 = \exp(-\Delta G_T{}^0/RT) = 4.6 \cdot 10^{-3}$ 1/MPa is small for a combustion temperature T_g = 2700 K, where $\Delta G_T{}^0 = -315.7 + 0.18T$ kJ/mole [10] is the standard Gibbs potential, p_{CO_2}, p_{CO} are the equilibrium pressures. Under equilibrium conditions, the yield of the product (TaC) is slight. Total conversion of tantalum into TaC is possible upon draining CO_2 from the particle surface.

The Boudoir reaction proceeds on the carbon surface

$$C_{(s)} + CO_{2\,(g)} \rightleftarrows 2CO_{(g)}, \qquad (5)$$

$\Delta G_T{}^0 = 172.5 - 0.176T$ kJ/mole [10]. For T_g = 2700 K, $\Delta G_T{}^0 = -302.2$ kJ/mole, $K_e = 7.1 \cdot 10^4$ MPa, i.e., this reaction proceeds sufficiently completely.

Since the CO_2 pressure above the tantalum surface is considerably higher than above the carbon surface (Fig. 2), CO_2 diffusion from the Ta surface to the carbon occurs in the specimen pores. The diffused CO_2 dissociates according to the reaction (5) and returns to the Ta surface in the form of the CO molecules that interact with it in conformity with the reactions (1)-(3). Therefore, the reactions (1)-(3) and (5) form a closed cycle in which the carbon is transported from the particles of solid carbon material (reagent) to the tantalum particles by CO molecules while the oxygen atoms are returned by CO_2 molecules. The reaction

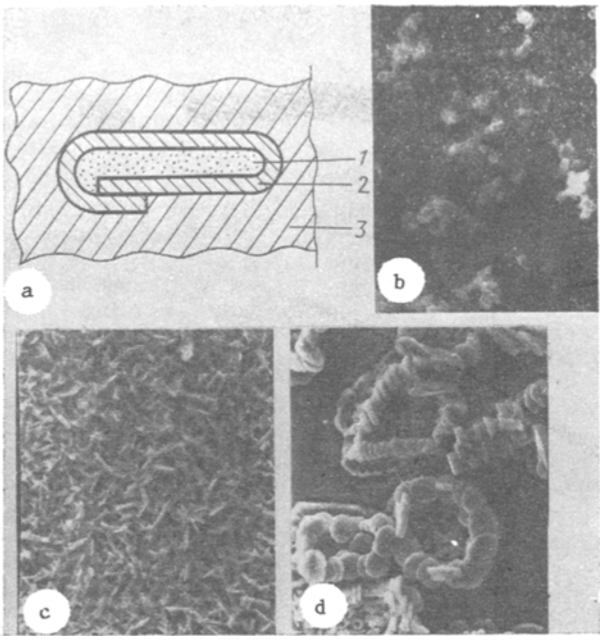

Fig. 4. Influence of tantalum surface treatment on interaction in model Ta + C cells under combustion wave conditions: a) diagram of the reaction model cell (1 – carbon material (soot, graphite, diamond, or carbon whiskers); 2 – tantalum foil; 3 – reaction charge (Ta + C); b) inner surface of unpolished foil after synthesis, ×10,000; c) inner surface of oxidized foil after synthesis, ×4000; d) outer surface of polished foil after synthesis, ×6000.

$$\mathrm{Ta} + \mathrm{C} \rightleftharpoons \mathrm{TaC},\ \Delta G_T^0 = -143{,}2 + 0{,}0049T\ \mathrm{kJ/mole}\ [10], \qquad (6)$$

is a result of the cycle, where $K_e = 3.4 \cdot 10^{10}$ for $T_g = 2700$ K, and the carbide layer is formed over the whole tantalum surface.

Tantalum transport can be realized by the volatile oxides TaO_2 and TaO, however, the intensity of this transport is insignificant as compared with the carbon transport because of the low partial pressures of the gaseous oxides (Fig. 2).

Sampling the gas directly from the hot Ta + C specimen is realized for an experimental determination of the gas phase composition. To this end, a 1-mm-diameter channel was drilled out to half the length along the specimen axis. The HTS was realized in an argon stream at atmosphere pressure. The gases emerging from the channel during combustion were colleced in a previously evacuated glass ampul. The gas samples were investigated on a mass-spectrometer.* In addition to the main component, argon, all the samples studied contained up to 10% CO. The CO_2 content was two orders of magnitude lower ($\leq 0.1\%$). No hydrocarbons were detected. The hydrogen content was not determined in these tests.

Therefore, the results of model investigations, investigations of specimens with a quenched front, thermodynamic computations, and experiments to determine the gas phase composition are in good agreement with each other and are described qualitatively by the proposed model of gas-phase transport. Apparently processes on the surface of the reagent particles are the limiting stage of the reaction cycle including the gas transport, and not diffusion in the gas. Indeed, even at 30 MPa pressure and the combustion temperature, the CO molecule diffuses in a 1-μm length within a very short time $\sim 3 \cdot 10^{-7}$ sec. It hence follows that the process rate should depend strongly on the state of the reagent surface

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*The authors are deeply grateful to N. V. Kir'yakov for conducting the mass spectrum analysis of the gas samples.

and, particularly, on the content of small quantities of surfactants in the mixture. This deduction was confirmed by experiments.

The main nongasificating impurity that can be concentrated on the tantalum particle surface in the powder under investigation is the iron impurity (up to 0.3 mass %). The dependence of the combustion rate of the Ta + C mixture on small additions of iron in the initial mixture is shown in Fig. 3a. Small quantities of the additions permit neglecting the change in the specific heat liberation associated with dilution of the charge. At the same time, investigation of the element distribution in the burning specimen showed that the iron is concentrated on the surface of the underreacting tantalum particles (Fig. 2b and c). Precisely the surface activity of the iron probably specifies a strong change in the combustion rate. It is interesting to note that washing off the tantalum powder in hydrochloric acid results in an abrupt (1.5-2 times) drop in the combustion rate.

Model tests were executed to investigate the sensitivity of the processes under consideration to the state of the tantalum surface. Pieces of 40-μm thick tantalum foil were polished mechanically and bombarded by argon ions and then some of them were oxidized in air at a 800-1000°C temperature for several seconds. Afterwards, closed 5 × 5 mm bundles were fabricated from the foil, within which a thin layer of carbon material was placed (Fig. 4a). These model "cells" were pressed in a reactive charge and synthesis was performed. The inner surface of the "packet" was investigated by using a scanning electron microscope. It turns out that the results of the experiment depend on the characteristics of the carbon material and on the state of the tantalum foil surface. Diamond powder (2-3 μm particle size) in contact with the cleansed tantalum surface manifested the least reactivity, interaction traces were not detected. The initial state of the metal surface plays the governing role in tantalum contact with PM-15 soot. In the case of utilization of polished foil subjected to ionic etching (cleansing), there is no interaction product in practice. If the foil for the model cell was not subjected to preliminary cleansing, finely dispersed particles of product (Fig. 4b) occur on its inner surface after SHS (Fig. 4b). Finally, a continuous layer of product of a golden tinge (Fig. 4c) is formed in the foil surface cleansed and then subjected to oxidation.

The nature of the interaction depends also on the temperature of the contact surface. The temperature on the outer foil surface turned toward the reaction charge is evidently higher than on the inner surface. Consequently, even on the polished outer surface "islets" of the product of interaction with an unusual microstructure are formed on the polished outer surface (Fig. 4d). Therefore, the results of model experiments and tests on the insertion of iron additions in a charge are in agreement with the deduction made above that tantalum and carbon interaction is limited by processes proceeding on the metal surface.

The aggregate of known and newly obtained experimental facts indicates that the model of "pure" reactive diffusion [11, 12] should be supplmented by analysis of the gas-phase transport and the processes proceeding on the surface. Reactive diffusion is just one of the important combustion stages of a mixture of tantalum and carbon powders of technical purity. It can be assumed that interaction in the solid-phase diffusion mode is realized in mixtures of especially pure, finely dispersed (≤1 μm) reagents with a large contact surface. Ideally, it is desirable to use powders of one reagent (Ta) clad by the other reagent (C) [1] for these purposes. Under conditions more approximate to technical synthesis, the presence of gasifying and surfactant impurities acquires values in principle. This confirms the deduction in [2] about the possibility of acting on the synthesis process by using a small quantity of gasifying additions, and also shows a new method for such an action, by using treatment of the reagent surface.

In conclusion, let us note that some of the results presented above indicate the presence of a small quantity of the liquid phase in the HTS wave. Among them is the presence of hollow shells in the produce (see Fig. 2c) (similar to the products of aluminum combustion in oxygen and carbon dioxide [13]) and of metallic "bonds" between TaC grains (Fig. 3). The results of thermodynamic computations (Fig. 2) also show the existence of liquid at a temperature of 2000°C and higher. The most probable reason for undermelting is the formation of the eutectics Ta—O and Ta—Fe since the oxygen and iron are fundamental impurities deteced in the tantalum powder (their content can reach 0.3%). The role of the liquid phase in the combustion and structure-formation process requires further study.

APPENDIX

Thermodynamic Analysis of the Gas Phase Equilibrium with Tantalum and Carbon during HTS

According to the Ta–O diagram [9], dissolution of oxygen in tantalum reduces the melting point: The melt L_1 is formed for an oxygen content of $x_\alpha = 0.057$ at. fractions in α-tantalum and T = 1880°C. Besides the reactions (1)-(3) on the tantalum surface, evaporation of the tantalum oxides occurs

$$[\mathrm{O}]_{\mathrm{Ta}} + \mathrm{Ta} \rightleftarrows \mathrm{TaO}_{(g)}, \tag{A.1}$$

$$2\,[\mathrm{O}]_{\mathrm{Ta}} + \mathrm{Ta} \rightleftarrows \mathrm{TaO}_{2(g)}. \tag{A.2}$$

The solid α-tantalum and the melt L_1 are considered ideal solutions. In conformity with the Ta–C phase diagram [9], we assume that carbon solubility in the α-Ta and L_1 phases is small, its excess is extracted in the form TaC by the reaction (2) and the carbon does not influence the chemical potential of the dissolved oxygen. The standard chemical potential of oxygen dissolved in α-tantalum $\mu_\alpha{}^0$ is determined by using the reaction $1/2\mathrm{O}_2 \rightleftarrows [\mathrm{O}]_{\mathrm{Ta}}$, $\Delta G_0{}^T = -383.09-0.0959T$ kJ/mole [9] and thermochemical constants [10]. The equilibrium pressures (Pa) for (3), (A.1), (A.2), and the reaction $\mathrm{CO}_{(g)} + \mathrm{Ta} \rightleftarrows \mathrm{TaC} + [\mathrm{O}]_{\mathrm{Ta}}$, which is the sum of reactions (1) and (2), are

$$\begin{aligned}
p_{\mathrm{CO}} &= 1{,}013\cdot 10^5\,[x_\alpha/(1-x_\alpha)]\exp(-49993{,}4/T+22{,}87),\\
p_{\mathrm{CO}_2} &= p_{\mathrm{CO}}\,x_\alpha \exp(-12019{,}96/T+1{,}133),\\
p_{\mathrm{TaO}} &= 1{,}013\cdot 10^5\,x_\alpha(1-x_\alpha)\exp(-66314{,}5/T+18{,}35),\\
p_{\mathrm{TaO}_2} &= 1{,}013\cdot 10^5\,(x_\alpha)^2(1-x_\alpha)\exp(-56413{,}3/T+19{,}39).
\end{aligned} \tag{A.3}$$

The total gas phase pressure is

$$p_0 = p_{\mathrm{CO}} + p_{\mathrm{CO}_2} + p_{\mathrm{TaO}} + p_{\mathrm{TaO}_2}. \tag{A.4}$$

Since $p_{\mathrm{CO}} \gg p_{\mathrm{CO}_2} \gg p_{\mathrm{TaO}}, p_{\mathrm{TaO}_2}$, then $p_0 \approx p_{\mathrm{CO}}$. To determine the standard chemical potential of oxygen in the melt, equilibrium lines of the phases α-Ta and L_1 on the Ta–O diagram [9] are approximated by straight lines. Then $\mu_{L_1}{}^0 = \mu_\alpha{}^0 + RT\varphi$, where $\varphi = \ln(7/12)$. The equilibrium pressures (Pa) with the melt L_1 are determined from (A.4) and the formulas

$$\begin{aligned}
p_{\mathrm{CO}} &= 1{,}013\cdot 10^5\,[x_{L_1}/(1-x_{L_1})]\exp(-52964{,}4/T+23{,}77+\varphi),\\
p_{\mathrm{CO}_2} &= p_{\mathrm{CO}}\,x_{L_1}\exp(-12019{,}96/T+1{,}33+\varphi),\\
p_{\mathrm{TaO}} &= 1{,}013\cdot 10^5\,x_{L_1}(1-x_{L_1})\exp(-63343{,}5/T+17{,}45+\varphi),\\
p_{\mathrm{TaO}_2} &= 1{,}013\cdot 10^5\,x_{L_1}^2(1-x_{L_1})\exp(-53442{,}3/T+18{,}49+2\varphi).
\end{aligned} \tag{A.5}$$

The reactions

$$\mathrm{TaO}_{(g)} + 2\mathrm{C}_{(s)} \rightleftarrows \mathrm{TaC}_{(s)} + \mathrm{CO}_{(g)}\ , \tag{A.6}$$

$$\mathrm{TaO}_{2(g)} + 3\mathrm{C}_{(s)} \rightleftarrows \mathrm{TaC}_{(s)} + 2\mathrm{CO}_{(g)} \tag{A.7}$$

and the Boudoir reaction (5) proceed on the carbon surface. The equilibrium pressures of the gases with carbon are determined from the relationships $K_e{}^{(A.6)} = p_{\mathrm{CO}}/p_{\mathrm{TaO}}$, $K_e{}^{(A.7)} = p_{\mathrm{CO}}{}^2/p_{\mathrm{TaO}_2}$, $K_e{}^{(5)} = p_{\mathrm{CO}}{}^2/p_{\mathrm{CO}_2}$ and the conditions $p_0 = p_{\mathrm{CO}} + p_{\mathrm{CO}_2} + p_{\mathrm{TaO}} + p_{\mathrm{TaO}_2}$, where $K_e{}^{(i)} = \exp(-\Delta G_T{}^0(i)/RT)$ is the equlibrium constant and $\Delta G_T{}^0(i)$ is the Gibbs potential of the i-th reaction.

The gas diffusion coefficient is $D = (1/3)\lambda\sqrt{8RT/(\pi m)}$, where the mean free path is $\lambda = RT/(\sqrt{2}\pi d^2 N_0 p)$, m is the molecular mass, $d = (2\text{-}3)\cdot 10^{-8}$ cm is the molecule diameter, p is the pressure, $D \approx 5$ cm^2/sec for CO and CO_2 for T = 2500°C and a $2\cdot 10^5$ Pa pressure, and $D \approx 1$ cm^2/sec for TaO and TaO_2, and $D_{\mathrm{CO}} \approx D_{\mathrm{CO}_2} \approx 0.2$ cm^2/sec for $p = 7\cdot 10^6$ Pa. The characteristic time of diffusion to the distance $h \sim 1$ μm is $\tau \sim h^2/D \sim 10^{-7}\text{-}10^{-8}$ sec for T = 2500°C and $p = 7\cdot 10^6$ Pa.

NOTATION

T, temperature; p, pressure; R, gas constant; $\Delta G_T{}^0$, standard isobaric–isothermal potential; K_e, equilibrium constant; x, dissolved oxygen concentration; μ^0, standard chemical potential; N_0, Avogadro number; D, diffusion coefficient.

LITERATURE CITED

1. A. G. Merzhanov, Self-Propagating High-Temperature Synthesis: 20 Years of Searches and Findings [in Russian], Preprint, Institute of Structural Macrokinetics, Academy of Sciences of the USSR, Chernogolovka (1989).
2. N. P. Novikov, I. P. Borovinskaya, and V. V. Boldyrev, Fiz. Goreniya Vzryva, 13, No. 3, 342-348 (1977).
3. V. M. Maslov, I. P. Borovinskaya, and A. G. Merzhanov, Investigation of Combustion Regularities and Mechanism of Titanium and Tungsten Powder Mixtures with Soot and Determination of the Optimal Conditions for Obtaining Solid Solutions by the HTS Method [in Russian], Preprint, Institute of Chemical Physics Branch, Academy of Sciences of the USSR, Chernogolovka (1978).
4. V. M. Shkiro, V. N. Doronin, and I. P. Borovinskaya, Fiz. Goreniya Vzryva, 16, No. 4, 13-18 (1980).
5. B. V. Stepanov, A. S. Mukas'yan, and K. G. Shkadinskii, Dokl. Akad. Nauk SSSR, 302, No. 1, 145-149 (1988).
6. V. M. Shkiro, G. A. Nersisyan, and I. P. Borovinskaya, Fiz. Goreniya Vzryva, 14, No. 4, 58-64 (1978).
7. A. S. Rogachev, V. M. Shkiro, I. D. Chausskaya, and M. V. Shvetsov, Fiz. Goreniya Vzryva, 24, No. 6, 86-93 (1988).
8. E. T. Turkdogan and T. W. Winters, Carbon, 8, No. 1, 39-53 (1970).
9. E. Fromm and E. Gebhardt, Gases and Carbon in Metals [Russian translation], Moscow (1980).
10. O. Kubashevskii and S. B. Alcock, Metallurgical Thermochemistry [Russian translation], Moscow (19820.
11. A. P. Aldushin, T. M. Martem'yanova, A. G. Merzhanov, et al., Fiz. Goreniya Vzryva, 8, No. 2, 202-212 (1972).
12. B. I. Khaikin, Combustion Processes in Chemical Technology and Metallurgy [in Russian], Cherogolovsk (1975), pp. 227-244.
13. P. F. Pokhil, A. F. Belyaev, Yu. V. Frolov, et al., Combustion of Powdery Metals in Active Media [in Russian], Moscow (1972).