The Convective-Conductive Mode of the Reaction Zone Propagation: A New Mechanism of Combustion of 'Gasless' Systems.

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Intense investigations of the process of combustion of the transition group metals (titanium, zirconium, hafnium, molybdenum) and non-metals (carbon, boron, silicon) began after A.G. Merzhanov, I.P. Borovinskaya, and V.M. Shkiro had discovered a new method of production of transition metal borides, silicides, and carbides in the combustion regime. The method was called self-propagating high-temperature synthesis, SHS. Small-size samples placed into the constant-pressure vessel were used in the first studies performed by the discoverers. It was shown that the combustion velocity, the structure and composition of the final products were independent of the external gas pressure [1-3].

. Therefore, this type of combustion and the systems were called 'gasless'. As found in the further studies, a small amount of impurity gases (30-60 cm^3 per 1 g of the mixture) released during combustion [4]. The processes of the impurity gas release were also shown to decrease the combustion velocity because of the sample continuity failure. On the base of the data of the experimental and theoretical studies, no principal changes in the specific features could be expected during the 'gasless' system combustion in the presence of one-way infiltration of the impurity gases (the sample was put into a gas-proof shell, *e.g*., a tube). Indeed, evaluation of the changes in the combustion temperature and velocity according to the theory of infiltration combustion showed that even under the condition of co-front infiltration of the impurity gases characterized by the maximum temperature rise the changes in the temperature did not exceed a few grades. These conclusions were also confirmed by the data obtained by numerical calculations for combustion of the condensed systems with gasifying additives [5].

However, unexpected results were obtained in the experiments on combustion of the gasless system titanium + carbon black at one-way infiltration of the impurity gases [6]. It was found that the increase in of the combustion velocity was anomalously high (up to 1.5 times) if the impurity gas could infiltrate through the green mixture only (co-front infiltration). The time-dependent changes in the velocity of the reaction front propagation were determined with the help of four thermocouples inserted into the sample composed of titanium-carbon black- polystyrene [7]. The velocity as found to continuously grow in all regimes. In the case of counter-front and bilateral infiltration, the increase was not high and constituted some 2-2.5 times. During combustion in the regime of co-front infiltration proceeding in a quite different manner, the front velocity was increased by 30 times for the time of the sample burning out (0.5 s) and mounted to 90 cm/s. The combustion process was of a nonstationary character typical for convective combustion [7].

The existing representations on the mechanism of gasless combustion do not provide explanation to a more-than-an-order increase in the velocity of the reaction front propagation as compared to that in the constant-pressure bomb. Since such basic problems as the necessary and sufficient conditions of occurrence of convective combustion of the 'gasless' systems, the mechanisms providing a positive reverse dependence of the combustion velocity and the impurity gas pressure, the limits of the combustion velocity

increase, the influence of the initiation parameters, have not been practically studied, they are the objectives of the present study.

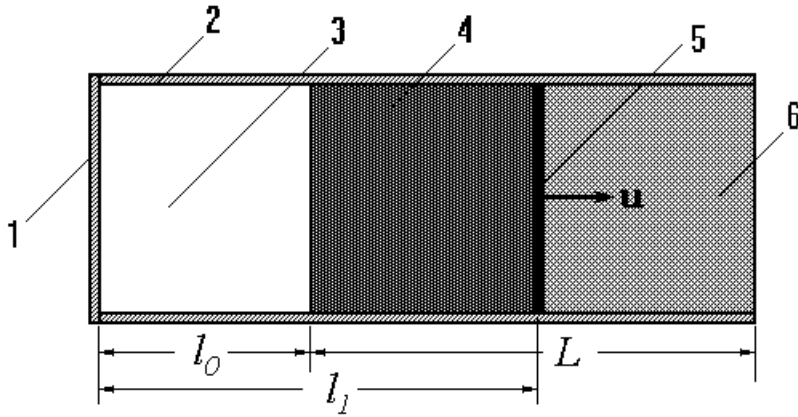The following model process is considered (see fig.1)

Fig. 1. The scheme of the process: 1 - a gas-proof lid; 2 - the reactor shell; 3 - the free volume (a gas-receiver); 4 - the condensed reaction products; 5 - the reaction zone; 6 - the green mixture.

The green mixture of the ρ_0 density and m porosity is placed into a tube reactor of the L length, with a gas-proof lid at one of the edges. After initiation from the closed edge, the combustion front is propagating along the green mixture. It is assumed that interaction of the mixture components results in the heat release (Q per 1 g of the mixture) and the impurity gas evolution ($\mathbf{m}$g per 1 g of the mixture). The combustion temperature is supposed to be higher than the melting point of one of the components and lower than the temperature of the final product melting. The impurity gas is evolved below the gas-impenetrable layer of the metal melt, which completely covers the reactor cross-section. The melt layer motion, which determines the front propagation, occurs due to the pressure gradient in the green mixture and the reaction products. It is believed that there is a free volume between the green mixture and the gas-proof lid. The existence of the free volume allows the account of the influence of the connecting pipes, the reader recesses, and other cavities formed under the actual conditions, on the combustion process.

Adequate mathematical description of the process of convective combustion of 'gasless' systems can be provided by combined consideration of the equation of balance of the gas mass in the burnt-out part of the sample and the equation describing the relationship between the front velocity, the pressure gradient, and the equation of the gas state. Since it is supposed that the conversion zone is expanded via a convective mechanism and the rate of interaction is determined by the process of heat transfer with the melt layer, the equation of the heat balance can be replaced with the thermal conductivity equation and the step-wise function can be used instead of the kinetics equation. The equation of the gas balance does not take into account the pressure distribution in the burnt-out part of the sample. The supposition on the absence of the pressure distribution is based on the experimental data on the high gas-permeability of the final products [6, 7].

The following set of equations describes the process of convective- ñonductive combustion:

$$\frac{dM_g}{dt} = u\mathbf{r}_0(1-m)\mathbf{m} \qquad (1)$$

$$\frac{dl_1}{dt} = u = u_{cond} + u_{conv} = u_{cond} + k(P_{gc} - P_{in}) \qquad (2)$$

$$M_g = l_0 \, \mathbf{r}_g + (l_1 - l_0)\mathbf{r}_g m_1 \qquad (3)$$

$$\mathbf{r}_g = \frac{P_{gc}}{RT_c} \quad ; \qquad T_c = T_{in} + \frac{Q}{C} \qquad (4)$$

The initial conditions:

$t = 0:$ $l_1 = l_0$; $u = u_{cond}$; $P_{gc} = P_{in}$,   (5)

Distribution of the sample temperature and conversion depth are of a step-wise character :
$T = T_{in}, \mathbf{h} = 0$ - in the initial state($L + l_0 > l > l_1$), $T = T_c = T_{in} + Q/c, \mathbf{h} = 1$ - in the condensed products($l < l_1$).

In accord with the experimental data [4,6,7] it is assumed that the impurity gas mass is much less than that of the green mixture, *i.e.* $\mathbf{r}_0(1-m)\mathbf{m}_1 << \mathbf{r}_0(1-m)$ èëè $\mathbf{m}_1 << 1$, and the maximum gas pressure in the pores of the condensed products**,** that can be createt by the impurity gas is much more then the initial pressure inside the reactor

$$\mathbf{r}_0(1-m)\mathbf{m}_1 RT_c / m_1 = P_{g\,max} \quad >> P_{in} \qquad (6)$$

where:M_g is the instantaneous gas mass behind the reaction front per unit of the cross-section area; l_0 is the length of the region inside the reactor free of the green mixture; l_1 is the distance from the gas-proof lid to the reaction front; t is the time, u is the reaction front velocity; u_{cond} is the front propagation velocity at conductive heat transfer(the u_{cond} value can be considered as the parameter of the model, since the reaction zone temperature is constant during the process); K is the coefficient of proportionality in the combustion law; ρ_0 and m are the green mixture density and porosity, respectively, m_1 is the porosity of the condensed products, μ_1 is the mass of the gas formed at burning out of 1 g green mixture; R is the universal gas constant; P_{gc} is the gas pressure behind the reaction front; P_{in} is the initial pressure inside the reactor; P_{gmax} is the gas pressure behind the reaction front calculated for the case when the gas released remains in the pores of the burnt sample; T_{in} is the initial temperature; T_c is the temperature of the condensed and gaseous products.

At the initial stage of the combustion process, when the length of the burnt-out layer $l_1 - l_0 \leq l_0$, the gas pressure P_{gc} behind the melt front and the combustion velocity u can be presented as

$$P_{gc} - P_{in} = u_{cond} / K * (exp(tKm_1 P_{g\,max} / l_0) - 1) \qquad (7)$$

$$u = u_{cond} \, exp\left(tKm_1 P_{g\,max} / l_0\right) \qquad (8)$$

where $P_{g\,max} = \mathbf{r}_0(1-m)\mathbf{m}_1 RT_c / m_1$ is the maximum gas pressure in the pores of the condensed products formed.

As seen from (7) and (8), the characteristic time of the convective combustion development t_*, when the pressure gradient and the combustion velocity are increase by e times, is

$$t_* = l_0 / Km_1 P_{g\,max}$$

The l_0 and P_{gmax} can be determined in the independent experiments, while the K value is found only in the experiments on the green mixture combustion at directed impurity gas infiltration.

Besides the approximate analysis, numerical solution of the initial set of equations was performed to determine the region of applicability of the results obtained by the approximate analysis and to see the time-dependent changes in the development of the convective combustion mode in the 'gasless' systems.

System (2)-(5) was transformed to a non-dimensional form for sake of the simplicity of the numerical analysis, reduction of the independent variables, and universality of the results obtained.

The following non-dimensional variables and parameters were used:

$$\overline{P}_{gc} = \frac{P_{gc}}{P_*}, \quad P_* = P_{g\,max}, \quad t = \frac{t}{t_*}, \quad t_* = \frac{L}{KP_{g\,max}}, \quad \overline{l}_0 = \frac{l_0}{L}, \quad \overline{l}_1 = \frac{l_1}{L}, \quad \overline{u} = \frac{u}{L/t_*}.$$

Fig. 2. The time dependence of the combustion velocity for $l_0 < 1$ (a) and $l_0 > 1$ (b) at $u_{max} = 0.01$ and $m_1 = 0.6$.
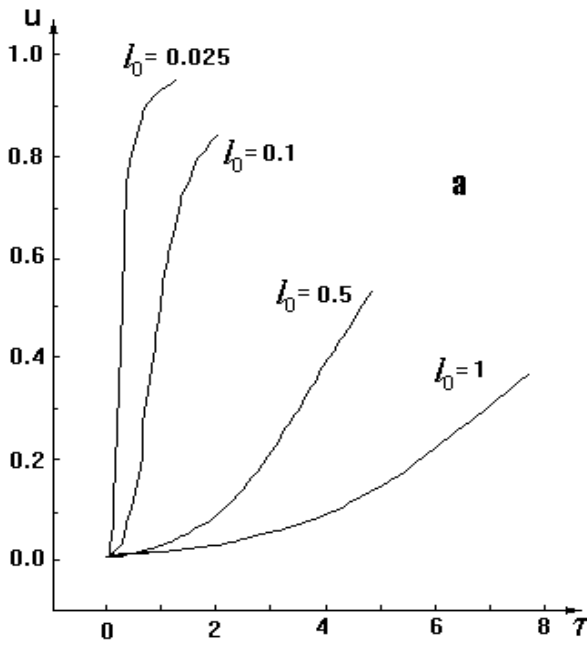
Figures 2a and 2b show the time dependence of the velocity of the reaction zone propagation for various values of parameter $\overline{l}_0$.

At low values of $\overline{l}_0$ ($\overline{l}_0 \leq 0.5$), the stage of fast (exponential) growth of the combustion velocity is seen to come to the end and turn to the mode with a slowly-changing velocity.

The numerical value of the velocity is close to a maximum attainable one:

$$\overline{u}_{max} = (\overline{P}_E - \overline{P}_{in}) + \overline{u}_{cond},$$

where $\overline{P}_E$ is pressure inside the reactor (the sample + the free volume) after complete burning out of the sample

$$\overline{P}_E = \frac{1 + \overline{l}_0 / m_1 * \overline{P}_{in}}{1 + \overline{l}_0 / m_1} \approx \frac{1}{1 + \overline{l}_0 / m_1}$$

For the high $\overline{l}_0$ values ($\overline{l}_0 \geq 1$), the process of combustion proceeds at a continuously growing velocity. The absence of an inflection point on the $u(\tau)$ dependence (like in the case of $\overline{l}_0 < 0.5$) implies that at $\overline{l}_0 > 1$ both the front velocity and acceleration are increased during combustion, as it follows from formulas (7) and (8).

The difference in the specific features of combustion in the co- and counter-front regimes of infiltration and the close coincidence of the combustion velocities at counter-front and
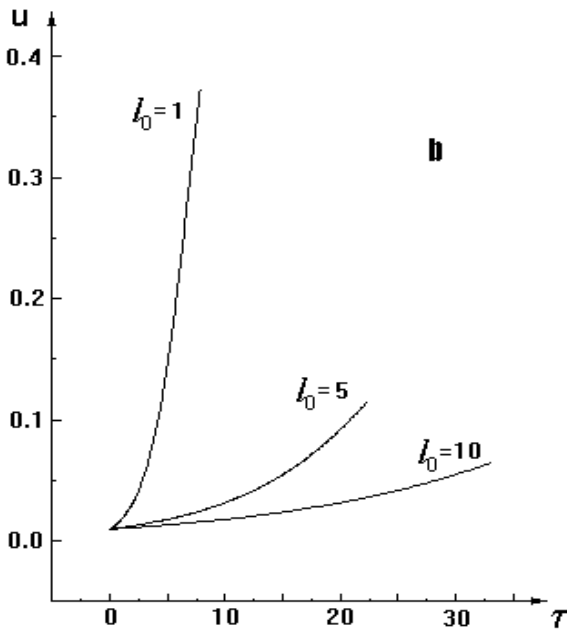
bilateral infiltration observed at combustion of the titanium-carbon black [6] and titanium-carbon black-polystyrene [7] mixtures are well explained within the model proposed. Indeed, under the model conditions the free volume of $l_0 \approx L$ corresponds to two latter regimes, *i.e.* during combustion the P_{gc} value is not practically changed and the characteristic time of development of the convective combustion regime $l_0/m_1 KP_{gmax}$ can be higher than the time of the sample burning-out. Hence, $u(L) \geq u(l_0)$. At the sample combustion in the co-front infiltration regime, the free volume l_0 is much less than the entire volume of the reactor L, therefore the characteristic time of development of the convective combustion regime $l_0/m_1 KP_{gmax}$ is low as compared to the time of the sample burning-out. Consequently, combustion proceeds in the convective regime characterized by a sharp (exponential) increase in the velocity of the reaction front propagation.

Conclusions

1. The physical and mathematical models of convective combustion of 'gasless' systems have been developed for the conditions of directed infiltration of the impurity gases.

2. It has been shown that at the impurity gas release the convective mechanism of combustion can be provided only by the motion of the melt layer of one of the reagents under the action of the impurity gas pressure.

3. It has been found that at the initial stage of combustion the growth of the front velocity and the gas pressure is of an exponential character.

4. It has been shown that some free volume at the reactor bottom is needed for occurrence of an accelerating regime of combustion.

5. The necessary and sufficient conditions of occurrence of the convective regime of the 'gasless' system combustion have been formulated.

6. Analysis of the proposed model provides explanation to the experimentally observed difference in the specific feature of the 'gasless' system combustion at counter-front, co-front, and bilateral infiltration of the impurity gases.

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