NONUNIQUENESS OF STATIONARY STATES IN COMBUSTION OF MIXTURES OF ZIRCONIUM AND SOOT POWDERS IN HYDROGEN

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It has been shown theoretically [1] that in complex systems, where chemical transformation can proceed along competing channels, the nonstationary states of combustion are not unique. Which of two possible, in the region of nonuniqueness, combustion states will be realized is determined by the conditions of ignition. Ignition from a high-temperature source leads to realization of a high-temperature regime, while ignition from a low-temperature source leads to the low-temperature regime.

Interesting objects of experimental investigation, from the point of view of clarifying the nonuniqueness, are systems of the type Me-C-H₂, in which interaction is possible along two mutually exclusive channels:

Me +
$$x$$
C + H₂ $\xrightarrow{\text{MeC}_x + \text{H}_2 \to \text{MeC}_x \text{H}_{1-x} + \frac{1+x}{2} \text{H}_2}$, (1)
Me + x C + H₂ $\xrightarrow{\text{MeH}_2 + x \text{C}}$.

It is shown in [2] for the example of the system $Ti-C-H_2$ that reactions (1) and (2) differ considerably with respect to the rates and temperatures of combustion and that this does not permit them to proceed simultaneously. The transition from one regime to another occurs abruptly when critical values of the parameters of the process are reached (the ratio C/Ti, hydrogen pressure, etc.).

The purpose of this work was to clarify the question of the existence of nonuniqueness of regimes accompanying the combustion of a three-component system of zirconium-carbon-hydrogen. The high-temperature source consisted of burning tablets consisting of the mixture Ti + 2B ($T_c \approx 3000\,^{\circ}\text{C}$), and the low-temperature source consisted of titanium tablets burning in hydrogen ($T_c \sim 1000\,^{\circ}\text{C}$). The intermediate case of ignition from a burning tablet consisting of the mixture Mo + 2Si ($T_c \approx 1700\,^{\circ}\text{C}$) was also examined.

Table 1 presents values of the rates and temperatures of combustion, as well as the phase composition of combustion products of mixtures of zirconium with soot for three different cases of ignition. As is evident from the data in the table, for ignition from a low-temperature source, all the compositions investigated burn in the low-temperature regime with the formation of zirconium hydrides. When tablets consisting of the mix-

TABLE 1

P _{H2} ,	Ignition from Ti+2B, T _C ≈3000°G		m Ti+2B, 000°C	Ignition from Mo + 2Si, Ignition from Ti + H ₂ , $T_{c} \approx 1700^{\circ}C$ $T_{c} \approx 1000^{\circ}C$	
	cm/ sec	r _c , °c	phase	$\begin{bmatrix} u_{C'} \\ cm' \end{bmatrix} T_{C'} \circ C $ phase $\begin{bmatrix} u_{C'} \\ cm' \end{bmatrix} T_{C'} \circ C $ phase	
$\mathrm{Zr}+0.7\mathrm{C}$					
5	1,8	2400	ZrC_xH_{1-x}	1,8 2400 ZrC _x H _{1-x} 0,6 850 ZrH ₂	
10	1,8	2400	ZrC_xH_{1-x}	0,85 930 ZrH ₂ 0,83 930 ZrH ₂	
40	1,75	1170	ZrH_2	1,8 1170 ZrH ₂ 1,8 1180 ZrH ₂	
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10	2,0	2900	ZrC_xH_{1-x}	2,1 2900 ZrC _x H _{1-x} 0,8 900 ZrH ₂	
30	2,0	2900	$ZrC_{xH_{1-x}}$	1,25 1100 ZrH ₂ 1,25 1100 ZrH ₂	
90	1,9	1250	ZrH_2	$ 1,95 1250 ZrH_2 2,0 1260 ZrH_2$	
				m Zr + C	
5	2,2	3200	ZrC		
20	1 '	1 1			
90	2,2	3200	ZrU	2,1 3200 ZrG 1,5 1230 ZrH ₂	

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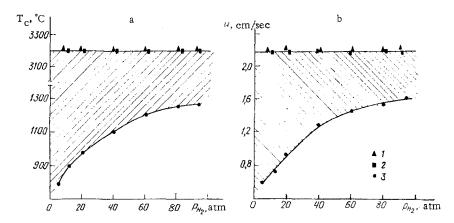


Fig. 1. Dependence of temperature (a) and rate of combustion (b) of mixture with composition Zr + C on hydrogen pressure: 1) ignition from $Ti + 2B (3000 ^{\circ}C)$; 2) ignition from $Mo + 2Si (1700 ^{\circ}C)$; 3) ignition from $Ti + H_2 (1000 ^{\circ}C)$.

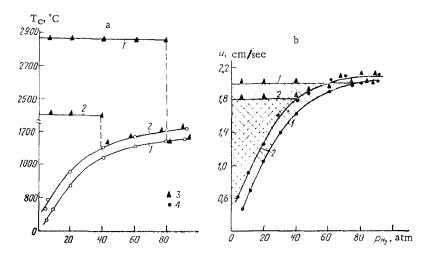


Fig. 2. Dependence of temperature (a) and rate of combusion (b) of mixtures with compositions Zr + 0.9 C (1), Zr + 0.7 C (2) on hydrogen pressure: 3) ignition from Ti + 2B (3000°C); 4) ignition from $Ti + H_2$ (1000°C).

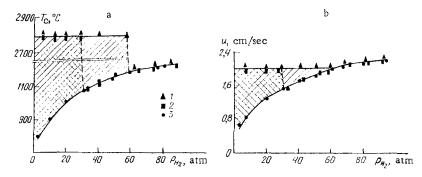


Fig. 3. Dependence of temperature (a) and velocity (b) of combustion of mixture with composition Zr + 0.8 C on hydrogen pressure: 1) ignition from Ti + 2B (3000°C); 2) ignition from Mo + 2Si (1700°C); 3) ignition from Ti + H₂ (1000°C).

tures Ti + 2B and Mo + 2Si are used as the sources of ignition, the mixtures of the stoichiometric composition Zr + C burn in the high-temperature regime with the formation of zirconium carbohydrides. For mixtures with a lower content of carbon (C/Zr = 0.7-0.9), under conditions of strong and intermediate ignition,

critical phenomena are observed — replacement of combustion regimes, and, in addition, in the case of ignition from tablets consisting of the mixture Mo + 2Si, less rigid critical conditions than in the case of ignition from the mixture Ti + 2B are required. Thus, for ignition from Ti + 2B, the critical value of the hydrogen pressure for a mixture with composition Zr + 0.7 C equals 40 atm, but for ignition from the mixture Mo + 2Si it equals 5 atm.

Figure 1 shows the dependence of the temperatures and rates of combustion of the composition Zr + C on the hydrogen pressure in two cases of ignition. It is evident that in the entire range of pressure investigated there exists a region of nonuniqueness of the combustion regimes. Figure 2 shows the same dependences for the compositions Zr + 0.7C and Zr + 0.9 C. In this case the region of nonuniqueness is limited; at $p_{H_2} = 40$ and 90 atm, respectively, the combustion regimes change, and, in addition, with the transition to the composition with the lower content of carbon, the region of nonuniqueness becomes narrower.

Figure 3 shows the region of nonuniqueness for the case of combustion of the mixture with composition Zr + 0.8 C using three sources of combustion. It is evident from the figures that with the transition from the high-temperature source to the source with intermediate temperature, the region of nonuniqueness of the combustion regimes is also observed to become narrower.

Thus, the theoretically predicted nonuniqueness of stationary regimes of combustion and the critical transition from the high-temperature regime to the low-temperature regime using ignition sources with different temperature are observed experimentally in the combustion of zirconium-carbon-hydrogen systems.

LITERATURE CITED

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GAS-DYNAMIC STRUCTURE OF FLAMES NEAR THE LIMITS OF FLAME PROPAGATION

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The dynamics of gas flow in comparatively rapidly burning gaseous fuel systems has been studied quite completely experimentally [1] and theoretically [2]. Qualitative and quantitative agreement has been obtained between theory and experiments on the form of the flame and the behavior of streamlines of the starting mixture and of the combustion products. The gas-dynamic structure of flame motion in near-limiting mixtures has practically not been studied, although it may be assumed that it is this particular structure that determines the considerable difference in the characteristic rates of combustion under terrestrial conditions and under weightless conditions (according to data in [3], flames burn five to ten times more slowly under weightless conditions). An indirect confirmation of the importance of gas-dynamic factors in the propagation of flames in near-limiting mixtures follows from the results of the numerical solution [4] of the exact Navier—Stokes equations for the reacting gas under conditions of natural convection. However, the physical picture of the intensification of combustion under conditions of natural convection remains unclear.

To obtain more detailed information on the gas-dynamic structure of a flame near the limits of propagation, we investigated the combustion of a number of near-limiting gaseous fuel mixtures using semischlieren motion picture photography. For the basic object of the investigations we chose the flame of the decomposition of acetylene, since it was expected that the soot formed with its combustion would permit visualizing in a natural manner the flow pattern of combustion products. The combustion of acetylene was investigated with initial pressures varying from 1.75 to $2.6 \cdot 10^5$ Pa.

The experiments were performed in a chamber, simulating "free" space, and in rectangular channels with dimensions $65 \times 65 \times 250$ mm. The chamber consisted of a rectangular steel parallelepiped with useful volume $250 \times 250 \times 65$ mm, equipped with windows consisting of optical glass, which permitted observation of the

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