EXPERIMENTAL OBSERVATION OF THE NONUNIQUENESS OF STATIONARY COMBUSTION IN SYSTEMS WITH PARALLEL REACTIONS

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It has been shown [1] that the interaction of a three-component titanium–carbon–hydrogen system can proceed by two parallel reactions:

$$\mathrm{Ti} + x\mathrm{C} + \mathrm{H_2} \begin{cases} \nearrow \mathrm{TiC}_x + \mathrm{H_2} \rightarrow \mathrm{TiC}_x\mathrm{H}_{1-x} + \frac{1+x}{2}\mathrm{H_2}, \\ \searrow \mathrm{TiH_2} + x\mathrm{C}. \end{cases}$$

The first reaction is characterized by high combustion velocities (2.2 cm/sec) and the formation of titanium carbohydrides with the general formula TiC_xH_{1-x} as a product, while the second is characterized by low combustion velocities (on the order of 1.3 cm/sec) and the formation of titanium hydrides as a result of the synthesis. The realization of one or the other branch of the reaction depends on a number of factors such as the hydrogen pressure, the carbon content of the initial mixture, the density of the pellet, the dispersion of the titanium powder, etc. It should be noted that the transition from one regime to the other occurs rapidly, with tiny changes in the parameters, so that in a given case it is possible to speak of the existence of some critical conditions for changes in the combustion regimes [1].

Theoretical studies have shown [2] that systems with parallel reactions may have a region with nonunique solutions, where the stationary combustion velocity depends on the ignition conditions for other conditions equal. Thus, ignition by a high-temperature source will create a high-velocity wave propagation regime and yield a certain product, while a low-temperature source will cause a low-velocity regime with formation of a different product.

TABLE 1

Burning mixture	p_{H_2}, atm	Ignition by a pellet made of				
		Ti+C		Mo+2Si		Ti powder
		I	II	I	II	I
Ti + 0,5C	3	2,1	$TiC_{0,5}H_{0,5}$	2,1	$TiC_{0,5}H_{0,5}$	0,4
	10	2,15	$TiC_{0,5}H_{0,5}$	0,6	TiH_2	0,6
	20	2,13	$TiC_{0,5}H_{0,5}$	1,2	TiH_2	1,25
	40	2,1	$TiC_{0,5}H_{0,5}$	1,4	TiH_2	1,37
	60	2,08	$TiC_{0,5}H_{0,5}$	1,55	TiH_2	1,55
Ti + 0,6C	5	2,18	$TiC_{0,6}H_{0,4}$	2,2	$TiC_{0,6}H_{0,4}$	0,8
	10	2,2	$TiC_{0,6}H_{0,4}$	2,23	$TiC_{0,6}H_{0,4}$	0,92
	20	2,18	$TiC_{0,6}H_{0,4}$	1,1	TiH_2	1,15
	40	2,2	$TiC_{0,6}H_{0,4}$	1,28	TiH_2	1,25
	60	2,18	$TiC_{0,6}H_{0,4}$	1,4	TiH_2	1,42
Ti + 0,7C	10	2,6	$TiC_{0,7}H_{0,3}$	2,5	$TiC_{0,7}H_{0,3}$	0,78
	20	2,5	$TiC_{0,7}H_{0,3}$	2,55	$TiC_{0,7}H_{0,3}$	0,8
	40	2,58	$TiC_{0,7}H_{0,3}$	1,1	TiH_2	1,1
	60	2,5	$TiC_{0,7}H_{0,3}$	1,3	TiH_2	1,32

Notes: (1) I) u, cm/sec; II) combustion product; (2) The combustion product from ignition by a titanium powder pellet is TiH_2.

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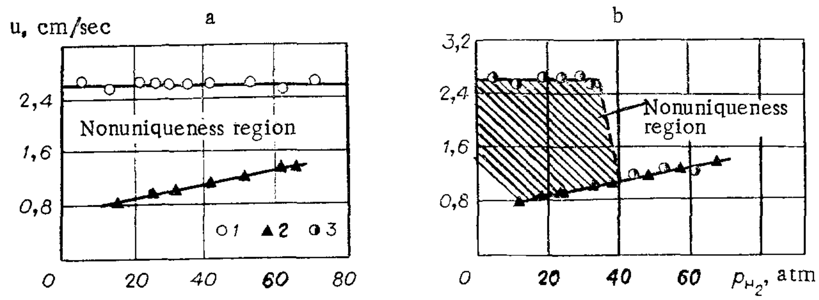

Fig. 1. Dependence of the combustion velocity on the hydrogen pressure for ignition by pellets of Ti + C (1), of Ti powder (2), and of Mo + 2Si (3).

Here the other parameters (gas pressure, particle sizes, pellet density) are the same for both cases.

In this paper we present some experimental data that confirm the theoretical conclusions about the nonuniqueness of stationary combustion. Our studies were made on a titanium–carbon–hydrogen system. The ignition sources were burning Ti + C pellets (T_c = 3200°K), and Mo + C pellets (T_c = 1900°K), or pellets pressed out of powdered titanium (with a combustion temperature in hydrogen on the order of 1200°K). The table lists data on the combustion velocities and phase composition of the combustion products from Ti + xC mixtures.

As the experiments showed, for low-temperature ignition only the hydride reaction mechanism occurs. It was not possible to initiate the carbidization reaction under these experimental conditions. When combustion was initiated with a high-temperature ignition source (Ti + C), only the carbidization reaction took place. In the intermediate case (ignition by Mo + 2Si pellet) the critical conditions were established under which the combustion regimes could change.

Figure 1a shows the dependence of the combustion velocity of a Ti + 0.7C mixture on the hydrogen pressure for high-temperature (Ti + C) and low-temperature (Ti) ignition. Over the entire pressure range studied here, a nonuniqueness region exists, but no critical phenomena were observed.

Figure 1b shows the combustion velocity as a function of the hydrogen pressure for the same composition but with ignition by pellets made of Mo + 2Si and Ti powder. It is clear that the nonuniqueness region is bounded, since for ignition by Mo + 2Si pellets there is a critical value of the hydrogen pressure above which the carbidization reaction cannot compete with hydride formation and the process can take place in only one direction.

Therefore, nonunique stationary propagation of the combustion zone depending on the ignition conditions is observed in three-component titanium–carbon–hydrogen systems. At the same time, one fact that has been neglected in the theory and requires further study should be pointed out: The experiment indicates that both the stationary regime of the combustion wave and the critical conditions for changes in that regime may depend on the ignition conditions.

LITERATURE CITED

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