

GASLESS COMBUSTION OF MIXTURES OF POWDERED TRANSITION METALS WITH BORON

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High-temperature self-propagating synthesis of inorganic compounds [1-3] has stimulated research in the principles and mechanisms of combustion of metal-nonmetal systems. Of special interest are systems with solid initial, final, and possibly intermediate components, examples of so-called "gasless" combustion, where the vapor pressure of all reagents and combustion products P at a combustion temperature T_c is much less than the external pressure p_0 . There is little information available on principles of combustion in such systems, most of it being contained in [4, 5].

Experimental characteristics of gasless combustion are the preservation of specimen weight after combustion, and independence of the combustion rate from inert gas pressure. The literature describes two systems satisfying these requirements: chrome-aluminum [4] and iron-aluminum thermites [5]. For iron-aluminum thermite, independence of reaction rate from inert gas pressure can be achieved only after dilution of the original mixture ($Fe_2O_3 + 2Al$) with a certain amount of the high-temperature reaction product (aluminum oxide) to the adiabatic combustion temperature of the mixture $T_{ad} = 2450^\circ K$ [5]. Without this dilution ($T_{ad} \approx 3000^\circ K$) the combustion rate of iron-aluminum thermite does depend on inert gas pressure [4]. A dependence of diluted system reaction rate on pressure can be observed by conducting experiments in a vacuum [6].

Determination of the vapor pressures of the components at the combustion temperature of iron-aluminum thermite diluted by aluminum oxide and chrome-aluminum thermite indicates that at pressures not too low both systems are of the gasless combustion type (Table 1).

The achievement of synthesis of a number of refractory inorganic compounds (carbides, borides, silicides, etc.) by combustion of transition metals with solid nonmetals (carbon, boron, silicon) has significantly increased the number of known gasless combustion systems, and permitted study of "gasless" combustion with models simpler than the thermites - combustion of pure elements.

Calculations reveal that because of the low vapor pressures of reagents and products at the combustion temperature, mixtures of powdered metals of the IV-VI groups of the periodic system with boron are examples of gasless combustion (Table 2).

This present study is an experimental investigation of certain principles in the combustion of mixtures of powdered transition metals (titanium, zirconium, hafnium, niobium, tantalum, molybdenum) with boron in an inert gas atmosphere. The effect of the combustion parameters on formation of the desired end products is also studied.

Methods and Purpose of Experiment

The experiments used powdered metals with dispersion $< 50 \mu$, purity not less than 99.5%, amorphous boron with particle size 0.1μ (98%), and also crystalline boron (UNIKhIM, Sverdlovsk) with dispersion $< 50 \mu$, purity 98%.

The experiments were performed with cylindrical specimens pressed from mixtures of the powdered metals and boron to a relative density of 0.2-0.7, determined by division of the absolute density of the specimen (ρ) by a factor corresponding to the maximum powder density ρ_{max} .

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TABLE 1

Reaction No.	Reaction	T _{ad} , °K	Component vapor pressure, mm Hg			
			Me ₂ O ₃	Al	Al ₂ O ₃	Me
1	(Fe ₂ O ₃ +2Al) + 0.88×Al ₂ O ₃ → 2Fe + 1.88 Al ₂ O ₃	2450	80*	310 ^[8]	5 ^[9]	31 ^[10]
2	Cr ₂ O ₃ +2Al → 2Cr+Al ₂ O ₃	2100	1†	29 ^[8]	1 ^[9]	5 ^[8]

† Calculated by method of [7].

† Estimated by comparison of known oxide vapor pressures and boiling and melting points from literature.

TABLE 2*

Reaction No.	Reaction	T _{ad} , °K	Component vapor pressure, mm Hg		
			Me	B	MeB ₂
1	Ti+2B → TiB ₂	3190	60	3	3·10 ⁻²
2	Zr+2B → ZrB ₂	3310	10 ⁻¹ †	4	5·10 ⁻¹
3	Hf+2B → HfB ₂	3520	5·10 ⁻¹ †	10	—
4	Nb+2B → NbB ₂	2330	3,5·10 ⁻⁵	2,8·10 ⁻²	—
5	Ta+2B → TaB ₂	2730	3·10 ⁻⁵	3,2·10 ⁻¹	10 ⁻¹
6	Mo+ B → MoB	1750	10 ⁻⁹	3,5·10 ⁻⁸	—

* Thermodynamic data for calculation of adiabatic combustion temperatures taken from [11]; reagent and boride vapor pressures from [8] and [12], respectively; vapor pressures of reagents in reactions 1-3 obtained by extrapolation of data of [12].

† Extrapolation of experimental data of [13] to combustion temperature gives values of 2.5 and 3.6 mm Hg for zirconium and hafnium, respectively.

TABLE 3

System	Spec. weight, g		Weight change, %
	before combustion	after combustion	
Mo+ B	5,82	5,80	0,34
	6,24	6,21	0,49
	5,49	5,46	0,55
Nb+2B	5,02	5,01	0,2
	4,83	4,81	0,41
	5,61	5,59	0,36
Zr+2B	3,59	3,56	0,89
	3,45	3,42	0,87
	7,02	6,95	1,0
Hf+2B	14,17	14,05	0,85
	13,41	13,90	0,82

TABLE 4

Original mixture	ρ _{rel}	Free boron content, % by wt.	Phase composition of combustion products
Nb+2B	0,21 0,5	0,24 0,10	NbB ₂
Zr+2B	0,25 0,5	0,13 0,09	ZrB ₂
Zr+ B	0,29 0,5	0,11 0,1	ZrB ₂ +Zr

$$\rho_{\max} = \frac{n_{\text{Me}} \cdot A_{\text{Me}} + n_{\text{B}} \cdot A_{\text{B}}}{\frac{n_{\text{Me}} \cdot A_{\text{Me}}}{\rho_{\text{Me}}} + \frac{n_{\text{B}} \cdot A_{\text{B}}}{\rho_{\text{B}}}}$$

where n_{Me} , n_{B} are the number of gram-atoms of metal and boron in the mixture; A_{Me} , A_{B} , ρ_{Me} , ρ_{B} are the atomic weight and density of the metal and boron, respectively. Specimens with a relative density $\rho_{\text{rel}} = 0.2-0.3$ (bulk) were reacted in quartz envelopes.

The experiments and reaction-rate measurements were performed by the method of [14] in a constant-pressure bomb at inert gas pressures of 1-150 atm. In some cases the reacted specimens were subjected to rapid quenching in liquid argon by the method of [3]. Reaction products were studied by chemical and x-ray analysis. The dependence of reaction rate and product composition on the following reaction

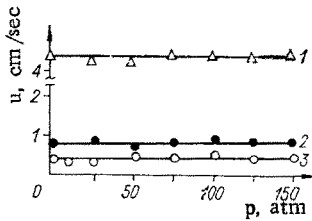


Fig. 1. Combustion rate of powdered metal-boron mixture versus argon pressure; $d = 1$ cm; $\rho_{rel} = 0.5$. 1) Ti + B; 2) Ta + B; 3) Nb + B.

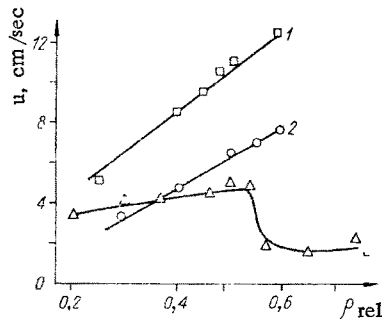


Fig. 2. Combustion rate versus specimen density, $d = 1$ cm. 1) Zr + 2B; 2) Zr + B; 3) Nb + 2B ($u \cdot 10$).

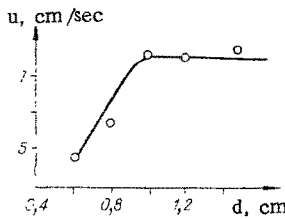


Fig. 3. Combustion rate versus Zr + B specimen diameter.

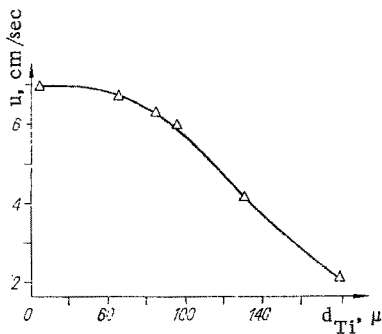


Fig. 4. Combustion rate of Ti + 2B mixture versus mean titanium particle size.

parameters was studied: inert gas pressure, specimen diameter and density, metal-particle diameter, dilution of mixture by end products. Specimens were weighed before and after combustion, and changes in form and dimensions were noted.

The experiments revealed that combustion of the mixtures occurred in two basic modes: equilibrium and auto-oscillatory. This was the first discovery of autooscillatory combustion in such systems and is partially described in [15].

Equilibrium Combustion

Figure 1 presents the results of combustion-rate measurements in mixtures of titanium, niobium, and tantalum with boron. As is evident from the figure, the reaction rate remains constant over the entire pressure range for all systems.

Specimens were weighed before and after combustion. Differences in weight were insignificant, not exceeding 1% (Table 3).

It is evident from the table that the greatest specimen weight change occurred in the systems Zr + 2B and Hf + 2B. It was assumed that these losses are connected with volatilization of small quantities of impurities, mainly boron anhydride B_2O_3 , which is always contained in the amorphous phase. Since the mixtures Zr + 2B and Hf + 2B have the highest burning temperatures (see Table 2), evaporation of the impurities occurs in a greater amount than in low-temperature systems such as Mo + B and Nb + 2B. In fact, replacement of amorphous boron by crystalline permitted reduction of the weight loss in Zr + 2B specimens to 0.5%.

Specimen shape after combustion varied for the different systems. Thus specimens of the low-temperature slow-burning mixtures Ta + 2B, Nb + 2B retained their form and dimensions after combustion, while specimens consisting of Ti + 2B, Zr + 2B, Hf + 2B increased in length during combustion by a factor of 1.5-2. This effect may be eliminated by increasing argon pressure to 70 atm or reducing the combustion temperature by dilution of the mixture with an inert substance. Just as is the loss in weight, the change in specimen dimensions is related to liberation of various impurities, in particular B_2O_3 . Evidence of this is that a specimen prepared by zirconium and crystalline boron did not change its dimensions during combustion, and introduction of boron anhydride into this system in an amount of 1-2% by weight led to noticeable lengthening of the specimen, although less than that when using amorphous boron.

Thus, the independence of reaction rate from inert gas pressure, low values of component vapor pressure at combustion temperature, and the insignificant weight losses, which can be attributed to evaporation of impurities, permit the conclusion that combustion of these systems occurs by the "gas-less" mechanism.

The effects of specimen density on reaction rate and product composition were studied in systems with significantly different reaction rates: fast-burning Zr + 2B, medium speed Zr + B, and slow-burning Nb + 2B. Results are shown in Fig. 2. The reaction rate of all three systems increases practically linearly with specimen density over the range $\rho_{rel} = 0.25-0.5$, with smooth motion of the combustion front. In

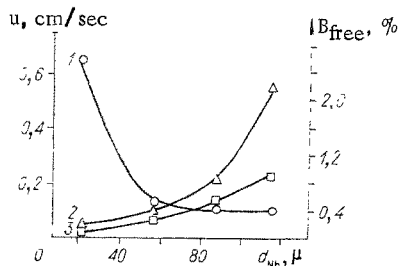


Fig. 5. Combustion rate of two-fraction Nb + 2B specimen (1), free boron content in quenched (2) and unquenched (3) specimens versus mean particle diameter of coarse fraction: $d = 1$ cm, $\rho_{rel} = 0.5$.

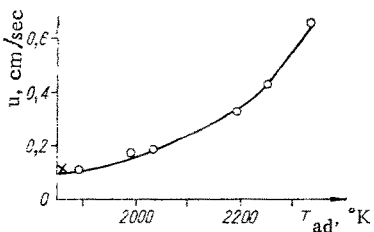


Fig. 6. Combustion rate of Nb + 2B mixture versus adiabatic temperature.

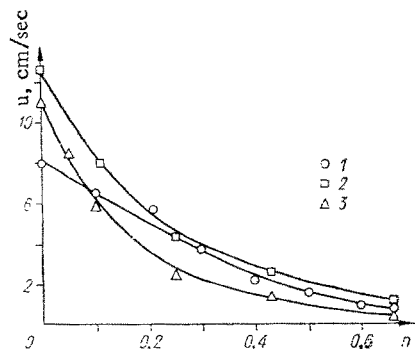


Fig. 7. Combustion rate versus quantity of diluent in original mixture (in moles per mole of boride obtained). 1) Ti + 2B; 2) Zr + 2B; 3) Hf + 2B.

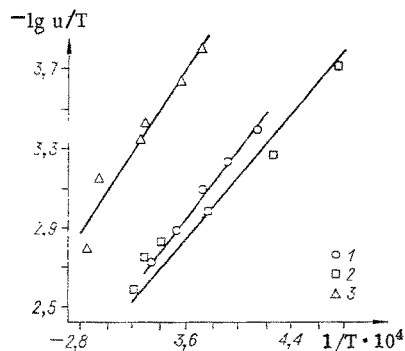


Fig. 8. Combustion rate versus adiabatic temperature. 1) Ti + 2B; 2) Zr + 2B; 3) Hf + 2B.

the system Nb + 2B with increase of specimen density to $\rho_{rel} = 0.55-0.65$ unstable phenomena develop, accompanied by a reduction in mean reaction rate.

As is well known, the density of the original mixture can have a significant effect on the degree to which a reaction goes to completion in solid systems. To verify this effect, reacted specimens were chemically analyzed for unreacted boron content, and the combustion products were also analyzed by x ray (Table 4). The data presented show that free boron content decreases with increase in specimen density; even at very low densities (bulk) combustion of the systems studied is quite complete.

The relationship of combustion rate and specimen diameter was studied in the system Zr + B. As follows from Fig. 3, at $\rho_{rel} = 0.6$ the combustion rate of this system increases with increase in specimen diameter, reaching a saturation region (adiabatic regime). The ratio of the threshold combustion rate to that corresponding to the adiabatic regime is 0.65.

Results of chemical analysis showed that change in specimen diameter over the range 0.6 to 1.5 cm had practically no effect on free boron content in the reaction products, which at this density did not exceed 0.1% by weight.

As is well known, real metal powders consist of groups of particles of different dimensions, and so a study of combustion in systems with different particle sizes of the components is of great interest. Figure 4 shows the burning rate of a Ti + 2B mixture as a function of titanium particle dimensions at a relative density $\rho_{rel} = 0.5$. The abscissa shows the mean values of the fractions with which the experiment was performed. For increase in particle size from 50 to 100 μ , a slight drop in combustion rate may be seen, while further increase in particle size causes a sharp drop in combustion rate.

Good information on the degree of completion of the metal-boron reaction in the combustion front and after its passage can be obtained from specially prepared mixtures containing various fractions of metal powders. Such experiments were performed with a Nb + 2B system. Mixtures were prepared with $\frac{2}{3}$ of the calculated niobium amount as particles $20 \pm 20 \mu$ in size, and $\frac{1}{3}$ consisting of particles 55 ± 15 , 85 ± 15 , or $115 \pm 15 \mu$ in size. It should be noted that mixtures in which all the niobium consisted of particles larger than $20 \pm 20 \mu$ did not react.

The reaction rate of niobium mixtures prepared with different fractions is presented in Fig. 5, curve 1. Addition of coarse niobium to the fine powder drastically (about $5 \times$) reduces the combustion rate; further change in combustion rate with increase in particle dimensions is insignificant. Figure 5, curves 2 and 3, indicates that in specimens quenched immediately after passage of the combustion front, the free boron content is 1.5-2 times as high as in unquenched specimens.

From this data it can be proposed that in the combustion front only the fine niobium fraction ($20 \pm 20 \mu$) enters the reaction completely, while the coarse fraction does not react, and acts to some degree as an inert diluent, reducing the combustion rate.

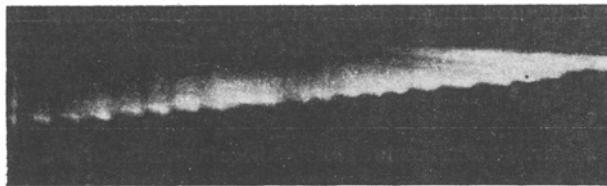


Fig. 9. Photograph of combustion of Nb + 2B; $d = 1.2$ cm; $\rho_{\text{rel}} = 0.6$; $u = 0.21$ cm/sec; $\nu = 2$ sec $^{-1}$.

To evaluate the amount of boron reacting with the coarse niobium fraction the degree of noncombustion $\varepsilon = B_{\text{free}}/B_{\text{tot}}$ was calculated (B_{tot} being the quantity of boron necessary for complete boridization of the coarse fraction). These values are presented below as a function of niobium particle diameter:

Original boron fraction, μ	Degree of noncombustion of quenched samples, %
20 ± 20	4
$\frac{2}{3}(20 \pm 20) + \frac{1}{3}(55 \pm 15)$	6
$\frac{2}{3}(20 \pm 20) + \frac{1}{3}(85 \pm 15)$	16
$\frac{2}{3}(20 \pm 20) + \frac{1}{3}(115 \pm 15)$	30

Comparison of this data with that for unquenched samples shows that the degree of noncombustion in the unquenched specimens is 1.5-2 times lower than in the quenched specimens. In other words, boridization of niobium occurs in two stages, combustion and postcombustion [16]. Results of chemical analysis of layers along the length of specimens also indicate the presence of a postcombustion stage. In the upper portion of the specimen* containing 100-130 μ niobium, the degree of noncombustion is significantly lower ($\varepsilon = 19\%$) than in the middle and lower portions ($\varepsilon = 33$ and 37% , respectively), i.e., the specimen continues to react after passage of the combustion front.

In light of the above, a correction can be introduced into the calculation of the adiabatic combustion reaction temperature for polydispersed niobium and boron.

Assuming that the fraction of coarse niobium ($\frac{1}{3}$) and the quantity of boron necessary for its boridization are inert diluents, we obtain a formula for calculation of T_{ad} :

$$(H_{T_{\text{ad}}} - H_{298})_{\text{NbB}_2} + 0.5(H_{T_{\text{ad}}} - H_{298})_{\text{Nb}} + (H_{T_{\text{ad}}} - H_{298})_{\text{B}} = (-\Delta H_{298}^0)_{\text{NbB}_2}.$$

The combustion temperature calculated by this formula is 1850°K.

Also calculated were combustion temperatures of the mixture Nb + 2B, diluted by its own product, niobium diboride. From these was constructed a curve of combustion rate versus calculated temperature (Fig. 6). It is easy to see that the point corresponding to combustion of the two-fraction mixture ($T_{\text{ad}} = 1850^\circ\text{K}$; $u = 0.1$ cm/sec) also lies on this curve, which confirms the assumption of inert behavior of the coarse niobium fraction in the propagation zone. (In accordance with the terminology introduced in [17], the propagation zone is understood to be that portion of the entire zone of transformation of initial substances into products wherein the processes are controlled by the combustion rate.)

The dependence of combustion rate and final product composition on quantity of inert diluent (final product) was also studied in Ti + 2B, Zr + 2B, Hf + 2B systems.

The results presented in Fig. 7 show that the reaction rate of all the metal-boron mixtures drops with increase of diluent in the original mixture. Chemical analysis of the combustion products showed that reduction in the burning temperature due to dilution does not affect the content of free boron in the product, its amount remaining within the limits 0.1-0.2%.

There exist no data in the literature on activation energy of the boride formation reaction at temperatures close to the combustion temperature. To determine such values, results of experiments measuring the reaction rate of mixtures diluted by the final product were used. It was assumed that in the mixtures Me + 2B (where Me = Ti, Zr, Hf) motion of the combustion front is described by the law for propagation of a combustion front in a homogeneous condensed medium [18]. In this case, assuming a first-order reaction, the experimental data should appear as straight lines in coordinates $\lg[u/T_{\text{ad}}], 1/T_{\text{ad}}$ [5], where u is

*Combustion propagated downward along vertically oriented specimens.

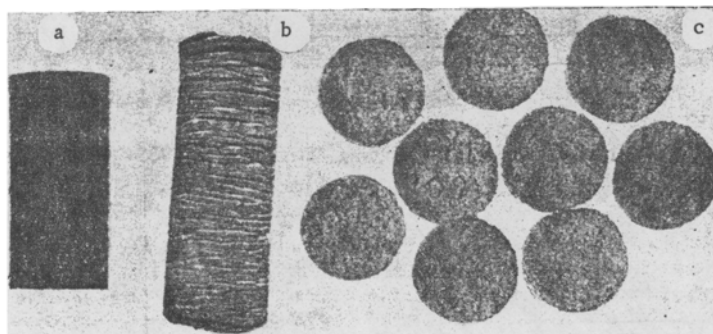


Fig. 10. Specimen of mixture Nb + 2B, $d = 1$ cm, $\rho_{rel} = 0.68$.

TABLE 5

Parameter	System									
	Ta+B		Ta+2B		Mo+B			Hf+B		
ρ_{rel}	0,53	0,64	0,4	0,63	0,24	0,43	0,62	0,18	0,64	
u , cm/sec	0,4	0,45	(Doesn't burn)	0,3	0,47	0,57	0,47	1,4	2,2	
ν , 1/sec	2	5	—	2,6	3	3	8	19	~80	

the reaction rate and T_{ad} the adiabatic combustion temperature. Processing of the data in these coordinates (Fig. 8) by the method of least squares gave the following activation energies:

Reaction	E, kcal/mole
Ti + 2B \rightarrow TiB ₂	76
Zr + 2B \rightarrow ZrB ₂	74
Hf + 2B \rightarrow HfB ₂	95

Autooscillatory Combustion

The experimental observation of an autooscillatory (pulse) mode of combustion of metal-boron powders was announced in [15]. We present below the results of an investigation of several principles of autooscillatory combustion.

A photograph of the autooscillatory combustion is shown in Fig. 9. The mean linear combustion rate (u) was calculated from the tangent of the slope of the trace to the horizontal, while the frequency (ν) was determined from the number of pulsations (teeth in the figure) per unit time. The spread of the ν values reached $\pm 30\%$. Specimens reacted in the autooscillatory mode retained their weight and dimensions, but consisted of layers formed by the pulsations, consisting of plane tablets equal to the specimen in diameter. For the various mixtures the tablets were either baked together, separable only with great difficulty, or easily separated, flaking by themselves and thus often increasing in height. Figure 10 shows individual tablets (c), and the specimen before (a) and after (b) burning. The tablet thickness, calculated from $\Delta h_c = u/\nu$, was close to that measured after combustion (Δh_m) (Fig. 11, curves 3 and 4). The somewhat higher values of Δh_m probably develop because of distortion of the shape of the tablet during combustion and cooling.

Experiments at $\rho_{rel} = 0.6$ and higher showed independence of the mean reaction rate and pulsation frequency from the external pressure; no characteristics of the autooscillatory combustion changed for an increase in argon pressure by a factor of eight.

Table 5 presents data on the characteristics of autooscillatory combustion for various mixtures and densities, specimen diameter being 1 cm. The minimum densities for each system were bulk densities.

More detailed studies of reaction rate and frequency were made with various mixtures of niobium* and boron (Figs. 12 and 13). With increase in density the frequency either does not change significantly

* The niobium powder had the following composition (by weight): 0.5% particles 160-200 μ ; 4.5%, 100-160 μ ; 20% 50-100 μ ; 75%, ≤ 50 μ .

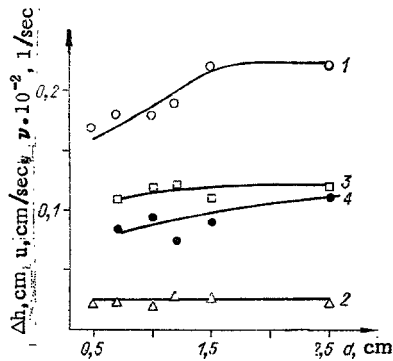


Fig. 11. Autooscillatory combustion characteristics versus specimen diameter; $\rho_{rel} = 0.6$. 1) u ; 2) ν ; 3) Δh_m ; 4) Δh_f .

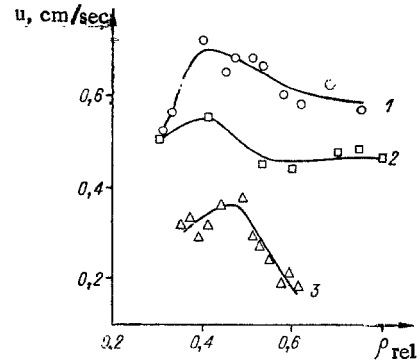


Fig. 12. Autooscillatory combustion rate versus density; $d = 1$ cm. 1) $3Nb + 2B$; 2) $Nb + B$; 3) $Nb + 2B$.

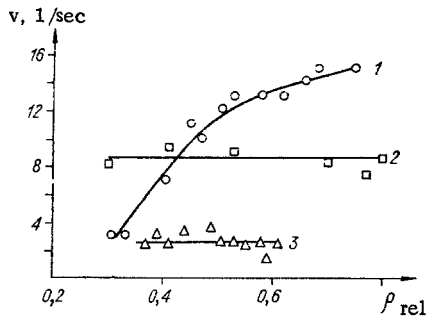


Fig. 13. Autooscillatory combustion frequency versus density; $d = 1$ cm. 1) $Nb + B$; 2) $3Nb + 2B$; 3) $Nb + 2B$.

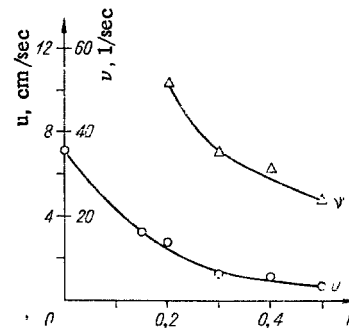


Fig. 14. Autooscillatory combustion characteristics of $Hf + 2B$ mixture versus dilution by reaction end product; $d = 1$ cm; $\rho_{rel} = 0.65$.

(compositions $3Nb + 2B$, $Nb + 2B$) or increases ($Nb + B$), while the combustion rates have a more or less sharp maximum. Chemical analysis of the specimens showed that for all mixtures studied, over the entire density range the free boron content did not exceed 0.2%. The degree of stratification of the reacted specimens decreased with decrease in density, and at densities equal or close to the bulk density tablet layers were not formed. Of the mixtures studied the most significant stratification occurred (in tablets which freely separated from each other) in $Nb + 2B$.

In experiments with combustion of $Nb + 2B$ at $\rho_{rel} = 0.6$, the effect of specimen diameter on combustion characteristics was insignificant (see Fig. 11, curves 1 and 2). At a diameter of 0.5 cm in most cases the specimens did not burn up completely. It is evident from Fig. 11 that in the autooscillatory regime $u_{lim}/u_{ad} \approx 0.8$ (u_{pr} at $d = 0.5$ cm, u_{ad} at $d = 1.5-2.5$ cm). This value is greater than that given by the theory of combustion limit proposed by Zel'dovich, according to which it should equal 0.61 [19]. According to [20] the limit of autooscillatory combustion is connected with extinction in depressions and corresponds to greater values of u_{lim}/u_{ad} than those of Zel'dovich's theory.

Using a mixture of $Hf + 2B$, the effect of reduction in combustion temperature by dilution with end product (HfB_2) on initiation and development of autooscillatory combustion was studied (Fig. 14).^{*} No pulsation was observed in the undiluted specimen. Near $n = 0.2$ equilibrium combustion changes to autooscillatory, and the specimen structure changes from spongy porous to stratified. Over the dilution range ($n = 0.2-0.5$) the frequency and velocity of autooscillatory combustion decrease.[†] The autooscillatory combustion observed in some specimens may have a thermal or a mechanical nature.

The thermal mechanism for autooscillatory combustion was examined theoretically in [21], where it was shown by calculation with an electronic computer that in combustion of homogeneous gasless compositions conditions may be created for the development of a stable pulse combustion regime. This burning mode is caused by an excess enthalpy at the combustion front, formed as a result of the small role of

^{*} The abscissa of Fig. 14 denotes n , the number of moles of HfB_2 diluent per mole of boride formed.

[†] The data presented in Fig. 14 were utilized earlier by Aldushin et al. [Fiz. Goreniya i Vzryva, No. 5 (1973)].

material diffusion as compared to heat transfer. It was found that the autooscillatory mode should be observed at $\alpha < 1$, the equilibrium mode at $\alpha > 1$, where

$$\alpha = \frac{cRT_{ad}^2}{0.4QE} (3.64 - Q/cT_{ad}).$$

Here R is the gas constant; Q and E are the thermal effect and activation energy of the chemical reaction; c is heat capacity.

It is evident from the formula that the transition from equilibrium combustion to autooscillatory may occur upon reduction of the combustion temperature, and that the autooscillatory regime is the preferred one for systems burning at the lower temperatures and, consequently, slowest reaction rates. It was shown in a study of pulsation dynamics [21] that the mean combustion rate and pulsation frequency decrease with removal from the limit of stability (reduction in α), and the structure of the pulsations becomes more complex. The stabilizing effect of a thermal flux of reaction products into the burning zone on the combustion process was also discovered.

Another cause for the development of pulsed burning can be considered – a mechanical one. This would be namely the periodic disruption of continuity (breakoff) of the specimen in the combustion front (in the unreacted material or the products) due to thermal and mechanical stresses or changes in the structure of the matter (for example, shrinkage upon burning). In this case the pulsed burning is a consequence of the layering, and not the contrary, as in the thermal mechanism.

We will compare the results obtained here with the data of [21], which considered the thermal mechanism of autooscillation development. Such a comparison can be only qualitative at present, because of the lack of sufficient experimental and reference data on kinetic and thermophysical characteristics of the systems considered, and also because of the lack in [21] of analytical relationships between the autooscillatory-mode parameters. According to [21], in the first place, this regime should be and is observed in gasless systems. Secondly, it is realized in systems burning at relatively low velocities and temperatures. For the systems considered here this velocity in the majority of cases is less than 1 cm/sec at $T_{ad} < 3000^\circ\text{K}$ (see Tables 2 and 5 and Fig. 12). Thirdly, in [21] the possibility of transition from equilibrium to autooscillatory burning with decrease in combustion temperature was proposed, just as was observed in the system Hf + 2B upon addition of a sufficient quantity of inert diluent (0.2 HfB₂) (Fig. 14). Fourthly, the oscillation frequency and combustion rate decrease with removal from the stability limit. For example, for Hf + 2B with an increase from 0.2 HfB₂ to 0.5 HfB₂ the oscillation frequency drops by a factor of two, and the combustion rate by a factor of four.

The complex character (with a maximum) of the dependence of combustion rate on density for niobium–boron mixtures (Fig. 12) may be explained in the following manner. Increase in specimen density produces greater layering of the combustion products. It is probable that the thermal flux from the combustion products, which affects the process significantly [21], decreases due to the reduction in effective thermal conductivity, which hinders increase in combustion rate and at high densities (strong layering) can even lead to its decrease. The greatest layering in reacted specimens observed in the Nb + 2B mixtures also produced the greatest reduction in reaction rate (Fig. 12).

The effect of layering on autooscillatory combustion frequency, which can also increase with increase in density (Fig. 13, curve 2) or remain unchanged (Fig. 13, curves 1 and 3), is thus quite complex. The degree of influence of layering on the combustion process is difficult to evaluate, since caking of the layers varies depending on composition and density of the mixture, and breakdown in continuity of the matter in the autooscillatory regime has not been studied theoretically.

No special study was made of the effect of particle dimensions on autooscillatory combustion. Above, in the discussion of equilibrium combustion, it was shown that replacement of fine particles by coarser ones decreased the velocity and temperature of the forward combustion zone. The autooscillatory mode was observed in mixtures of niobium with coarse particles. The lower combustion rate value and the very existence of the oscillatory regime stemmed from this fact. Development of autooscillatory combustion upon addition of coarse particles indicates primarily (together with factors such as incomplete combustion) that the effective kinetics of these systems correspond to strong braking of the reaction rate with penetration depth [17].

Using thermodynamic calculations of the combustion temperature [11] and the activation energy values, we estimate the value of the criterion α in the above formula:

Mixture	α
Zr + 2B	1.0
Ti + 2B	0.8
Hf + 2B	0.55
Hf + 2B + 0.2 HfB ₂	0.5
Hf + 2B + 0.5 HfB ₂	0.35

Considering the approximate nature of the kinetic and thermophysical characteristics, it can be considered that these data agree with experiment. Thus, for mixtures with $\alpha \approx 1$ (Zr + 2B, Ti + 2B) the auto-oscillatory regime was not observed, while for the diluted hafnium-boron mixture burning in the pulse mode the value of α was much lower ($\alpha \leq 0.5$).

The existence of autooscillation in Mo and Ta mixtures is interesting in that, according to thermodynamic calculations, the metal in such mixtures does not melt. There are at present no weighty facts in favor of the existence of mechanical autooscillation, while some experimental results seem to contra-indicate this possibility. If layering of the material occurred due to increase in density of reaction products and packing with shrinkage (density of the borides formed is 1.5-2 times as great as specimen density), this would be reflected more strongly in the low-density specimens, which was not observed in experiment.

The development of pulsations predicted by the theory of [21] and the layering of reacted specimens occurring upon dilution of the mixtures are more indicative of a thermal than a mechanical nature of auto-oscillation. With dilution, velocity and temperature of combustion are reduced, leading to reduction in temperature gradient and thermal stresses in the combustion front. The difference between properties of the unreacted mixture and final product also becomes less, together with related effects (shrinkage, etc.).

To sum up the above, it can be said that the available experimental data evidently indicate that auto-oscillatory combustion is a thermal mechanism. The effect of layering and possible disintegration of the specimen in autooscillatory combustion require special experimental and theoretical study.

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