CONCENTRATION STRUCTURE OF THE COMBUSTION WAVE IN THE TITANIUM–CARBON SYSTEM

V. M. Shkiro, V. N. Doroshin,
and I. P. Borovinskaya

For self-propagating high temperature synthesis of inorganic refractory compounds and in the development of the theory of exothermal reaction front propagation in heterogeneous systems, studies of combustion wave structure, degree of component conversion, and mode of combustion front propagation are necessary.

Earlier experimental and theoretical studies of high temperature synthesis systems have revealed a number of peculiarities in the combustion mechanism and have established the existence of regimes of incomplete reagent conversion into end products [1–4]. It has been shown that the absence of an ideal internal structure in the original systems and the presence of kinetic braking (due to formation of a product layer) lead to a different combustion wave structure. In contrast to the classical concepts developed by Zel'dovich and Frank-Kamentskii [5] this wave has a wider reaction zone, in which the degree of conversion is not equal to unity, and a burnup region [4, 6]. At the present time temperature profiles have been established experimentally for several heterogeneous systems [7], although concentration profiles have not yet been obtained. The question of the degree of reagent conversion in various combustion zones and the character of concentration change has also not been studied because of the intrinsic difficulties of studying combustion products by traditional methods.

In the present study, local x-ray analysis will be used to study conversion depth (change in component concentration) in the combustion wave as a function of the metal particle dispersion.

The system chosen for study was titanium–carbon, in which the presence of incomplete conversion regimes has been demonstrated [1, 3]. The stoichiometric mixtures were prepared from titanium powders and technical grade carbon (carbon black), brands PTS and PM-15TS, respectively. Particle dimensions were as follows: Ti, <45, 75–100, 120–160, 180–250; 120–160; C, ~0.1 (μm). The mass content of oxygen (%) comprised 0.3, 0.4, 0.4, 0.5, 7.3, and 0.3. The prepared mixture was poured into a cylindrical glass vessel ($\rho \simeq$ 1 g/cm^3) and placed in a container holding liquid argon so that only the upper face of the specimen with its attached tungsten filament remained above the argon surface. After the specimen was cooled to liquid argon temperature, combustion was initiated and the specimen was completely immersed in the liquid argon (Fig. 1). In the experiments the mixture did not burn over the full length of the specimen, since because of heat losses the combustion front ceased its motion and the combustion products were rapidly quenched. Because the boundary of the combustion wave was not clearly visible its propagation rate was not recorded.

After the experiment, the specimen was extracted from the container and soaked in a binder liquid (bakelite lacquer, shellac) to give it greater mechanical strength. This preparation made it possible to produce a longitudinal metallographic section (Fig. 2), needed to perform the local x-ray studies with the JXA-5A device. A zone about 1 mm in width was studied, passing through the specimen center for its entire length. It was decided to determine the change in concentration of titanium, by determining its concentration in ~50 μm steps along the specimen. The carbon concentration was determined by direct measurements and recalculation based on the measured titanium content in the compound TiC_x. The accelerating voltage used for the studies was 15 kV. Under these conditions the longitudinal and transverse localization (the region of electron excitation and characteristic x radiation were calculated after [8]) comprised 0.7 and 3 μm. Titanium concentration was determined at 20–30 points (5–10 particles) for each fixed level. Graphite, pure titanium, and stoichiometric titanium carbide were used as references. The concentration of titanium, carbon, and oxygen in the particles was determined by use of calibration curves, constructed by recording the intensity of the characteristic x radiation TiK_α, CK_α, OK_α with a flow-type counter from Ti, TiC, C (graphite), TiO_2 (rutile), SiO_2 (quartz), Si. Quartz and lead stearate were used as crystal analyzers. For the light elements (C and O_2) the accelerating voltage was 10 kV at a beam current of $2 \cdot 10^{-7}$ A.

Chernogolovka, Translated from Fizika Goreniya i Vzryva, Vol. 16, No. 4, pp. 13–18, July–August, 1980. Original article submitted February 6, 1978.

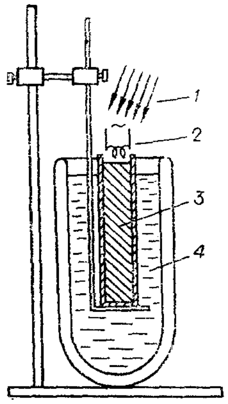

Fig. 1

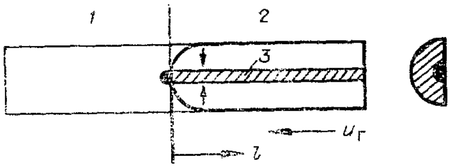

Fig. 2

Fig. 1. Diagram of "combustion front quenching" experiment; 1) gaseous argon draft; 2) tungsten filament; 3) specimen mixture in container; 4) Dewar flask with liquid argon.

Fig. 2. Diagram of section studied; 1) original mixture; 2) combustion products; 3) zone studied (width ~1 mm).

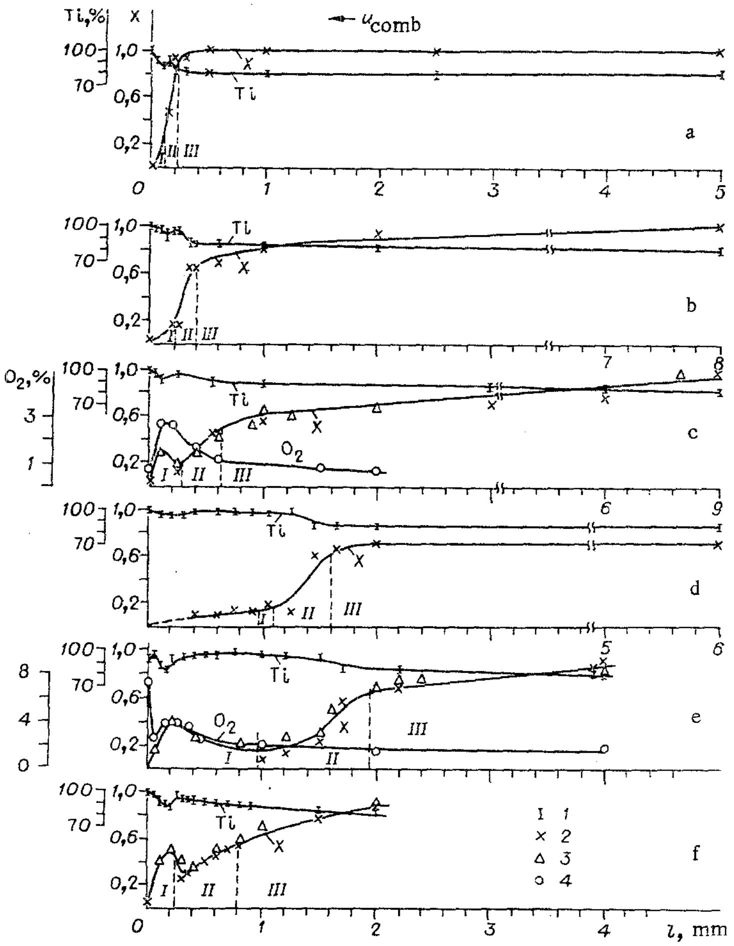

Fig. 3. Titanium, carbon, and oxygen concentrations vs. distance along specimen; I) heating zone; II) propagation zone; III) burnup zone. 1) Titanium concentration; carbon concentration: 2) calculation; 3) measurement; 4) oxygen concentration. a) $d_{Ti} \leq 45$ μm; b) $75 < d_{Ti} \leq 100$ μm; c) $120 < d_{Ti} \leq 160$ μm, O_2 0.4%; d) $180 < d_{Ti} \leq 250$ μm; $120 < d_{Ti} \leq 160$ μm, O_2 7.3%; f) $120 < d_{Ti} \leq 160$ μm ($p_{CO} = 1.25$ atm).

The experimental data obtained permitted a quantitative characterization and demonstration of the change in conversion depth within the front as a function of the size of the original metal particles.

Figure 3a-d shows titanium concentration in the specimen as a function of distance along the combusted specimen. The carbon concentration is denoted by X ($X = C/Me$, the atomic ratio of the TiC_x, $X_{max} = 1$, which is analogous to the depth of conversion). In the presence of wide reaction zones [4, 6] it is difficult to clearly separate the boundary of the propagation and burnup zones, so they are divided arbitrarily on the graphs (dashed line). The position of the beginning of the propagation zone was chosen by microscopic studies, as the point where fusion and flow of the metal particles was observed. For fine metal particles not exceeding 45 μm in size (Fig. 3a) the degree of conversion in the propagation zone is close to unity (~0.9), while the burnup zone in which maximum conversion is achieved is insignificant. With increase in metal particle size the width of the propagation zone increases, although the degree of conversion is lower than in the case of fine particles, and a significant portion of the material reacts in the burnup zone. In the mixtures with 75-100 and 120-160 μm particles conversion is completed at a larger distance from the propagation zone, and for the mixture with 180-250 μm titanium particles the final conversion depth does not reach a maximum (~0.7) because of heat losses. The increase in propagation zone and decrease in the completeness of reaction therein with growth in titanium particle size can be explained by the fact that with growth in particle size the inhomogeneities in component distribution in the mixture increase. The presence of the capillary flow effect [9] decreases these inhomogeneities only insignificantly, since with increase in particle size the flow time becomes greater than the reaction time. Thus, with expenditure of the component in short supply in a given segment, a major role begins to be played by transport of this component from the neighboring segment where it is in excess. In view of the low values of the diffusion coefficients and the effect of kinetic braking produced by the dependence of heat liberation on growth of the product layer [4], the degree of conversion in the zone of combustion wave propagation (and in the presence of heat losses, also in the extended burnup zone) may not reach a maximum.

An interesting effect recorded in these experiments is the presence of a titanium concentration minimum in a very narrow region in the preheating zone (Fig. 3a-d). The extent of this minimum in the preheating zone and the amount by which the titanium concentration changes are dependent on the size of the original metal particles. For fine particles (Fig. 3a) the width of this region comprises ~40 μm), but increases to 300 μm for metal particles 180-250 μm in size (Fig. 3d). The titanium concentration at this minimum then changes from 95 to 85% (by mass).

The presence of such a titanium concentration minimum in a very narrow region of the preheating zone does not correspond to existing concepts of combustion wave structure in this zone [4, 6]. It is probable that processes occur which lead to the formation of singular regions in the preheating zone. One of these may be interaction of the gases formed with the solid phase. It is known from the literature that in the process of combustion of "gasless" high temperature synthesis systems the generation and displacement from the hot into the cold zone of large quantities of gases in the form of CO, CO_2, H_2 is possible [10, 11]. Some of these gases, in our opinion, may react with the material present before leaving the reaction zone, as a result of which the titanium concentration in this region changes abruptly. It should be noted that the smaller the metal particle diameter, the greater is the decrease in titanium concentration, i.e., the more the gas phase effect manifests itself. This is apparently due to the fact that the rate of removal of gaseous products depends significantly on the porosity of the system. In fact, for systems with coarser fractions, where the porosity is significantly higher, the region of gas phase interaction is wider, and the reduction in titanium concentration is lower.

One of the gases responsible for this effect may be oxygen, present in the initial mixture in the form of an oxide film on the metal surface, and also as adsorbed oxygen on the surface of the carbon black particles. Data of chemical analysis (see above) indicate that the total oxygen content of the mixtures comprised 0.5-1.0%. To verify these propositions, an experiment was performed with a mixture containing titanium in the form of 120-160 μm particles with additional oxygen (7.3%). It developed that for the high oxygen content mixture this effect was expressed more clearly, i.e., the region was wider and the change in titanium concentration greater (Fig. 3e), with the metal concentration ahead of the propagation zone being higher than in the original mixture. According to chemical and local x-ray analysis, the original particles contained ~93% Ti, while ahead of the propagation zone the titanium content was ~97-99%. These data indicate that at high temperatures partial purification of the metal from impurities occurs in the combustion wave.

Additional local x-ray studies of oxygen distribution in the specimens showed that the maximum oxygen content is reached just at the point where gas phase interaction appears (Fig. 3c, e) while the concentration distribution has a number of peculiarities. For the mixture containing 7.3% O_2 (determined by pulsed heating in an inert medium and chromatography, 7.0% by local x-ray spectral analysis) there is initially a reduction in oxygen to 2.5% in the initial metal particles. This is related to the fact that at low temperatures reduction of Ti oxides by carbon probably occurs, with formation of CO and CO_2 which are subsequently partially removed from the specimen. With increase in temperature the oxygen concentration in the particles increases (2.6%) and reaches a maximum in the region of the gas phase effect (4%).

It is obvious that in the gas phase effect region the maximum concentration (pressure peak) of oxygen-containing gases occurs, both those which have not escaped from the specimen, and those arriving from higher temperature regions. Since the rate of gas removal depends on specimen porosity, while the solubility of oxygen (and carbon) in the system Ti−O, according to the state diagram of [12], increases with increase in temperature, there must occur in the gas phase effect region processes of solid phase carbidization with participation of the gas phase and solution of oxygen in the metal. Optical studies of metal particles in the gas phase effect and adjacent zones have shown that their surface has the gold-yellow and violet coloration, corresponding to the oxides TiO and Ti_2O_3. X-ray analysis of these particles in a DRON-2.0 machine confirmed the oxidation of the particle surfaces to TiO and Ti_2O_3. Further increase in temperature (close to the propagation zone) leads to a decrease in oxygen content in the particles.

An increased metal concentration in the particles after the gas phase effect region was observed for all the mixtures studied; the presence of carbon in the particles in the gas phase effect region is indicated by the fact that the sum of the Ti and dissolved oxygen concentrations is not equal to 100% (Fig. 3c: $\Sigma[Ti + O_2] \simeq 92.6\%$; Fig. 3e: $\Sigma[Ti + O_2] \simeq 87\%$). Direct measurements of the change in carbon concentration within the specimen showed that there is a significant carbon concentration in the gas phase effect region, which indicates the participation of the gaseous phase in the carbidization process. It is known from [13] that when titanium carbide is synthesized in a furnace with a CO atmosphere there is initially a maximum in carbidization rate, after which decarbidization occurs, while increase in CO pressure affects the process and testifies to the participation of the gas phase in carbidization.

In order to discover the influence of increased CO concentration on the effect of gas-phase interaction for a heating mixture of titanium and carbon, we conducted the experiment at a CO partial pressure of 1.25 atm in a bomb of constant pressure [14]. The glass flask with the titanium (particle size 120-160 μm, O_2 content 0.4%)−carbon mixture was emptied into a vessel containing liquid argon and was suspended from a thread such that after the mixture began to be heated the thread burned through the sample fell into the argon. In this case the mixture also failed to burn along its entire length (the method of preparing the metallographic microsection was described above). It is clear from the results presented in Fig. 3e that increase in the CO partial pressure leads to a stronger effect of gas-phase interaction: the stronger the change in titanium concentration, the wider the region of the gas-phase effect, according to extent of the heat front, and the greater the degree of carbonization in the region of the gas-phase effect. That is, as in the case of titanium carbide synthesis in furnaces, one observes the influence of the gas phase of the carbidizing process.

Thus, this study of combustion wave structure in the titanium−carbon system using local x-ray analysis has for the first time experimentally demonstrated the quantitative distribution of the reagents in the combustion front, the presence of incomplete reagent conversion in the propagation zone, and the existence of an extended burnup zone, in which significant reaction of the material may occur. Increase in metal particle size leads to a lower degree of conversion and expansion of the propagation zone. Studies of concentration profiles in the combustion front have shown qualitative correspondence of the results with existing theoretical concepts of the combustion mechanism in heterogeneous condensed systems [4, 6].

The effect of gas phase interaction in the combustion front, observed here for the first time, indicates that the gas phase products formed may have a significant effect upon, and participate directly in, the process of chemical interaction in the combustion front, i.e., their role does not reduce to a mere expansion of the reaction mass and change in thermophysical properties in the combustion front, as has been demonstrated for other systems in [11].

LITERATURE CITED

1. A. G. Merzhanov and I. P. Borovinskaya, Self-Propagating High Temperature Synthesis of Refractory Inorganic Compounds [in Russian], Ob. Inst. Khim. Fiz., Akad. Nauk SSSR, Shernogolovka (1970).
2. I. P. Borovinskaya, A. G. Merzhanov, et al., Fiz. Goreniya Vzryva, <u>10</u>, No. 1 (1974).
3. V. M. Shkiro and I. P. Borovinskaya, in: Combustion Processes in Chemical Technology and Metallurgy [in Russian], Ob. Inst. Khim. Fiz., Akad. Nauk SSSR, Chernogolovka (1975).

4. B. I. Khaikin, in: Combustion Processes in Chemical Technology and Metallurgy [in Russian], Ob. Inst. Khim. Fiz., Akad. Nauk SSSR, Chernogolovka (1975).
5. Ya. B. Zel'dovich, Zh. Fiz. Khim., 22, No. 1 (1948).
6. A. G. Merzhanov, Archives Comb. Proc., 5, No. 1 (1974).
7. T. S. Azatyan, V. M. Mal'tsev, et al., Fiz. Goreniya Vzryva, 13, No. 2 (1977).
8. I. B. Borovskii and V. I. Rydnik, in: Apparatus and Methods for X-Ray Analysis [in Russian], 5th ed., SKB-RA, Leningrad (1969).
9. V. M. Shkiro and I. P. Borovinskaya, Fiz. Goreniya Vzryva, 12, No. 6 (1976).
10. V. M. Shkiro, G. A. Nersisyan, and I. P. Borovinskaya, Fiz. Goreniya Vzryva, 14, No. 4 (1978).
11. V. I. Vershinnikov and A. K. Filonenko, Fiz. Goreniya Vzryva, 14, No. 5 (1978).
12. P. Kofstad, High Temperature Oxidation of Metals [Russian translation], Mir, Moscow (1969).
13. G. A. Neerson and O. E. Krein, Zh. Prikl. Khim., 25, 134 (1952).
14. N. N. Bakham and A. F. Belyaev, Heterogeneous Combustion of Condensed Systems [in Russian], Nauka, Moscow (1967).

STUDY OF THE COMBUSTION OF HAFNIUM – BORON MIXTURES BY OPTICAL PYROMETRY

V. A. Andreev, N. M. Mal'tsev,
and V. A. Seleznev

It follows from thermodynamic calculations that temperatures up to 4000°K are developed in the combustion of self-propagating high temperature synthesis gasless mixtures [1]. The combustion products of such compositions are in the condensed phase and possess very high values of radiation coefficient [2]. The combustion rate of the mixtures is independent of external pressure [3]. These facts indicate the possibility of using such mixtures as sources of radiation in the visible and IR range of the spectrum [4]. In connection with this, it is of interest to study the process of combustion of gasless mixtures and their temperature–energy characteristics: energetic luminance, temperature, combustion rate, radiation coefficients of combustion products.

The dependence of temperature and combustion rate on the ratio of components in the mixture, and also on the degree of mixture dilution by the end product permits determination of certain principles of the combustion mechanism and individual kinetic constants of the reactions which occur [5, 6]. The combustion products of such mixtures are refractory compounds. Their radiation coefficients at the temperatures which develop in the combustion wave are as a rule unknown, but knowledge of these values is of undoubtable practical interest [2].

The present study examined the system hafnium–boron. It was chosen because the combustion temperature of the stoichiometric composition Hf + 2B is 3520°K [1], one of the highest combustion temperatures occurring in systems used for self-propagating high temperature synthesis. Thus, one can expect the highest energetic luminance from this system. Upon combustion of the stoichiometric composition Hf + 2B hafnium diboride is formed [5]. It should be noted that in the combustion temperature calculation of [1] the value used for the enthalpy of formation $\Delta H^{298}_{\mathrm{form}} = -80$ kcal/mol. However the measured $\Delta H^{298}_{\mathrm{form}}$ of this compound in the high temperature synthesis process proved equal to −62.6 kcal/mole [7]. Calculation of the adiabatic temperature using the latter enthalpy of formation value gives a temperature of 3350°K. The combustion temperature of the stoichiometric mixture as measured by a thermocouple proved to be close to 3000°K [8].

Experimental Method. Mixtures with various ratios of metal to metalloid were studied. The atomic fraction of boron in the mixture (coefficient "a") was varied from 0.8 to 3. The stoichiometric mixture Hf + 2B, diluted by 10, 20, 30, and 40% (by weight) of the end product was also studied.

The mixtures were pressed in the form of cylindrical specimens 10 mm in diameter having a relative density of 0.6. Combustion was carried out in an inert atmosphere of argon at a pressure of 10 atm. In the experiments type GFM-1 TU-48-4-176-72 hafnium was used (particle size smaller than 15 μm), with purity not less than 98%; the boron was amorphous type MRTU6-02-292-64 (particle size less than 1 μm) of 97% purity; dispersion of the hafnium diboride diluent was less than 63 μm. The change with time of the temperature and energetic luminance of the surface layer of the burning mixture was determined in the experi-

---

Moscow. Translated from Fizika Goreniya i Vzryva, Vol. 16, No. 4, pp. 18–23. Original article submitted July 30, 1979.