Mechanisms of Pulsating Combustion During Synthesis of Advanced Materials

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Gasless combustion is a specific type of combustion, where all initial reactants, as well as intermediate and final products, remain in condensed (solid or liquid) state. This process is of great interest because of its prospective applications in combustion synthesis of advanced materials. The stability of combustion wave propagation is an important factor in determining the quality of materials produced by combustion synthesis. In this work, a digital high-speed microscopic video recording method is used for direct observation and quantitative characterization of pulsating combustion in several gasless systems. The experimental data quantitatively describe, for the first time, oscillations of local instantaneous velocity at length scale about 10 μm and time scale $\sim 10^{-3}$ s. Three systems investigated were: Ta-C, Nb-B, and Ti-C. Two new mechanisms of pulsating combustion were identified: crack-induced oscillations occur in Nb + B and Ta + C systems, while ignition-extinction oscillations take place during reaction in Ti + xC system.

Introduction

Combustion synthesis (CS) has generated notable interest due to its potential for producing advanced materials (Varma et al., 1998a). The process is characterized by extremely high heating rates (up to 10^6 K/s), high temperatures (up to 4,000 K), and short times of reaction completion (usually less than 1 s, sometimes even $10^{-3}-10^{-2}$ s). These characteristics, while attractive for the synthesis of unique compounds, also make it difficult to study the mechanism of reaction wave propagation, which is essential in order to form materials with tailored microstructures and properties.

Gasless combustion is a specific type of CS, where all initial reactants, intermediate and final products remain in condensed (solid or liquid) state. The general process can be described as follows. Initial reactants, typically in the form of fine (0.1–100 μm) powders, are mixed in the appropriate ratio and cold pressed into the sample (for example, rectangular or cylindrical shape). After initiation locally from one side of the sample, due to the high heat of product formation, a self-sustained reaction wave propagates in the form of a bright-glowing front (Figure 1). Examples of such processes are reactions of transition metals with carbon and boron such as

$$\mathrm{Ta + C = TaC + 146\ kJ/mol}$$

$$\mathrm{Ti + C = TiC + 230\ kJ/mol}$$

$$\mathrm{Nb + 2B = NbB_2 + 175\ kJ/mol}$$

The combustion wave propagation is not always steady. The stability of combustion wave propagation is an important factor in determining the quality of materials produced by CS. In order to produce uniform product, a stable combustion regime is desired. Furthermore, it is also important to know the boundaries where combustion, stable or unstable, can propagate. It is generally believed that instability effects during CS have essentially thermal origin and appear when the heat of reaction is insufficient to support stable motion (cf. Novozilov, 1992). Two main types of instability have been found for CS waves: one-dimensional (1-D) (pulsating mode) and 2-D (spin mode). The main features of such modes in gasless systems have been widely studied experimentally (cf. Merzhanov et al., 1973; Maksimov et al., 1981; Zhang and Munir, 1992). For example, in the case of pulsating combus-

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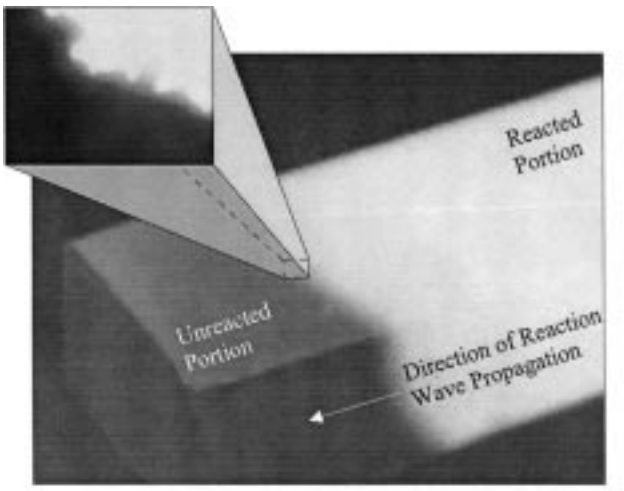

Figure 1. Combustion wave propagation in gasless system.

tion, it was found that the frequency of pulsating is commonly about $1-10^2 s^{-1}$, but values of approximately 10^{-2} s^{-1} have also been reported (Wenning et al., 1994). On the other hand, combustion theory predicts loss of stability with decreasing the specific heat of reaction or increasing heat losses, and various criteria have been suggested to determine conditions where stable combustion becomes impossible, that is, the reaction front cannot propagate with constant velocity (cf. Shkadinskii et al., 1971; Makhviladze and Novozilov, 1971; Matkowsky and Sivashinsky, 1978; Margolis, 1983). Generally, this may lead to either extinction or to formation of combustion modes propagating in an unstable manner. Specifically, the temperature space-time history for pulsating combustion was described theoretically by computer simulation (cf. Shkadinskii et al., 1971; Aldushin et al., 1973). However, detailed experimental studies of the combustion wave during this mode at different length and time scales have not been reported.

In the present work, we use a digital high-speed microscopic video recording (DHSMVR) method (Rogachev et al., 1994; Mukasyan et al., 1996) for direct observation and quantitative characterization of pulsating combustion in several gasless systems. Our main objective was to measure variations of instantaneous combustion velocity during the pulsating period and to *in-situ* study the microstructural details of the phenomena. The results provide new insight into the mechanistic causes of unstable combustion in gasless systems.

Experimental Procedure

Three systems were studied, which are known to react in pulsating combustion mode: Ta + C, Nb + B and Ti + xC (where x was varied in the range 0.4 to 1.0). Characteristics of the powders used in the experiments are listed in Table 1. The reactant powders were dry mixed in an appropriate ratio in a ball-mill, and were pressed into parallelepiped shaped samples with dimensions $30 \times 20 \times 5$ mm with various porosity in the range 40–60%.

The experimental setup is shown in Figure 2 (for details see Varma et al., 1998b). The sample is mounted into the chamber filled with Ar (purity > 99.996%) at normal atmospheric pressure, and an electrically heated tungsten wire initiates the reaction at one end of the pellet. The propagation of the reaction wave is observed through a quartz window using a long-focus microscope (K-2, Infinity) attached to a digital high-speed video camera and processor. The spatial resolution of the microscope is 1.7 μm, while magnification may be varied from 50 to 800 times, with the corresponding viewable area varying from 0.15 to 25 mm^2. The high-resolution high-speed black and white video camera (Kodak EktaPro 1000 Imager) attached to the microscope records the events and the images are transferred to the digital processor (Kodak EktaPro Hi-Spec Motion Analyzer). The recording rate varies from 50 to 12,000 frames/s. Using the computer access interface, the digital images can be transferred directly to the computer and analyzed to yield quantitative characteristics of the reaction wave structure, including brightness map, local curvature and instantaneous velocity. The principles of video image treatment are described elsewhere (Mukasyan et al., 1996).

To observe the microscopic mechanism of reaction front propagation, we selected a small area in the middle of the sample and applied the DHSMVR technique to record the reaction wave while it passed through this area (see also Figure 1). Magnification was selected to provide the observation of two to five pulsating periods, which allowed both to make precise measurements of the instantaneous velocity of the combustion front U as well as to observe the microstructural evolution of the reaction medium.

Table 1. Characteristics of the Reactant Powders

Powder	Size, μm	Purity, %	Vendor
Ta	5	99.9	Cerac
Nb	< 5	99.5	Aesar
Ti	< 44	99.5	Cerac
C (lampblack)	0.1	99.8	Fisher
B (amorphous)	0.1	98	Russia

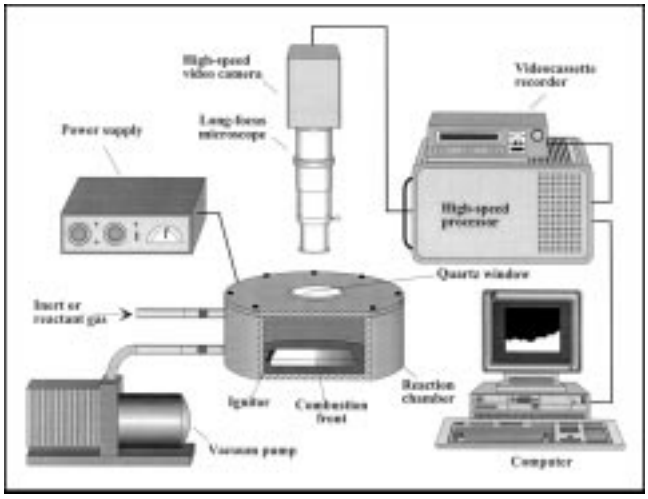

Figure 2. Digital high-speed microscopic video recording (DHSMVR) technique.

Experimental Results

Systems Nb + B and Ta + C

Oscillating combustion mode was observed in these systems even for highly exothermic stoichiometric mixtures (Nb + B, $T_{ad} = 2250$ K; and Ta + C, $T_{ad} = 2{,}740$ K). Characteristic dependencies of the reaction front location as a function of time for the Nb + B system are shown in Figure 3. Note that horizontal plateaus indicate periods of hesitation, when no movement of the combustion front occurs ($U = 0$). It may be observed that the duration of the hesitation is about 10–100 ms and the oscillations are more evident for low dense samples (compare curves 1 and 2). After hesitation, propagation occurs during which U (slope of the curve) changes smoothly; upon initiation, the velocity remains essentially constant but increases just prior to the next hesitation. Thus, the relatively steady propagation occurs over distance about 1 mm with relatively high velocity (for example, approximately 1.5 cm/s for low density sample).

The experimental result that U increases just before the hesitation indicates that extinction does not occur due to heat losses. Indeed, if lack of heat generated by the combustion reaction is the reason for front halting, the velocity must decrease before the moment of hesitation. The reason why the front stops becomes clear from the sequence of DHSMVR frames, which show the process of structure transformation during combustion (Figure 4a). It can be seen from these microscopic patterns that cracks form periodically just ahead of the combustion front, resulting in hesitation of its movement. During the hesitation period, unreacted mixture at the opposite side of the crack is preheated by the heat flux (mainly radiation, but also convective and conductive heat transfer through the gas and random ''bridge'' contacts) from the hot product. At some critical condition, the unreacted mixture ignites and the cycle repeats. Additional evidence of the cracks is provided in Figure 5, where micro pictures of investigated area made by the DHSMVR technique before and after reaction are shown. These pictures clearly indicate crack formation at the locations of reaction front hesitation. Thus, we may refer to this kind of oscillation as a *crack-induced oscillation.*

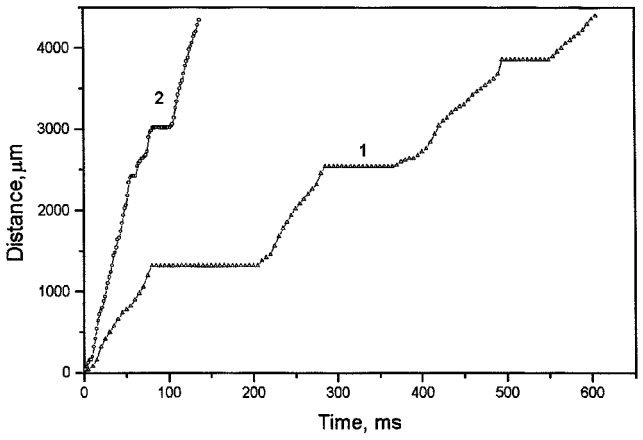

Figure 3. Characteristic dependencies of the reaction front location as a function of time in Nb + B system for samples with different relative density.

1: $\rho = 0.55$; 2: $\rho = 0.69$.

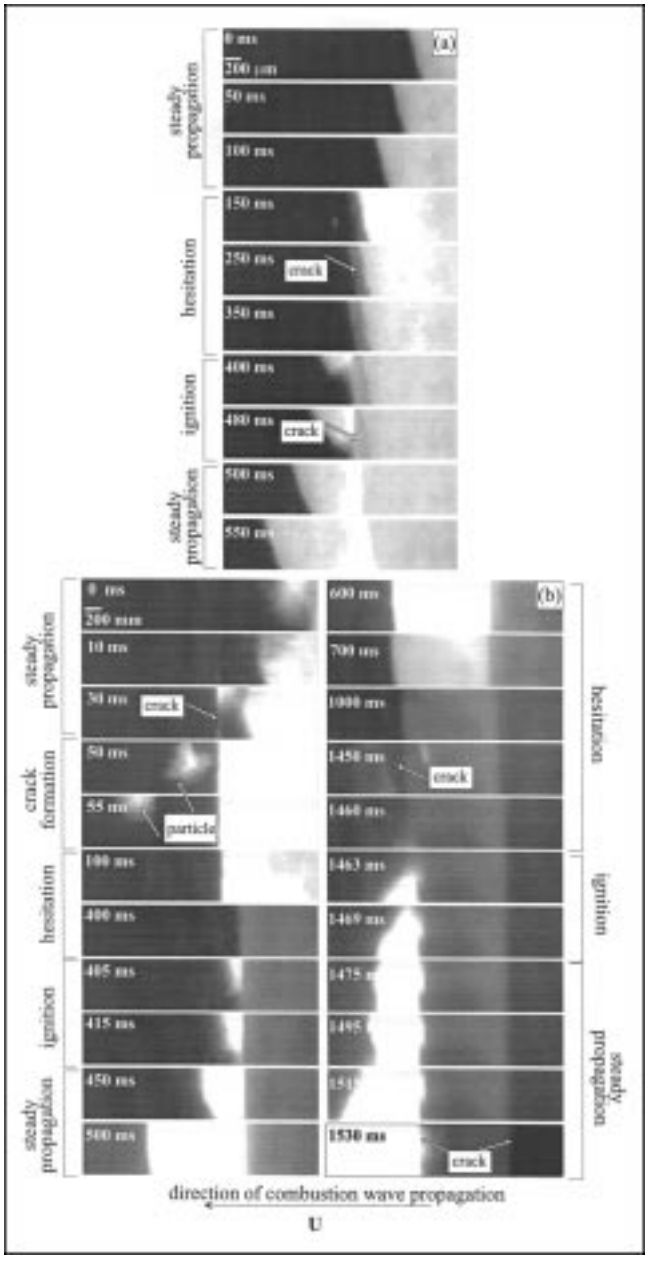

Figure 4. Sequences of video images illustrating microstructures of combustion wave.

(a) Nb + B system; (b) Ta + C system.

It is interesting that the behavior of the front, when it approaches the crack (that is, increase of U), is similar to that when the front approaches the end of the sample (Varma et al., 1992). The mechanism of crack formation is not fully clear yet. The most probable reason for crack appearance is impurity gas (mainly H_2 and CO) generated at the combustion front (Merzhanov et al., 1997). This gas, released in the pores at high temperature, creates inner pressure sufficiently high to fracture the sample along the combustion front plane.

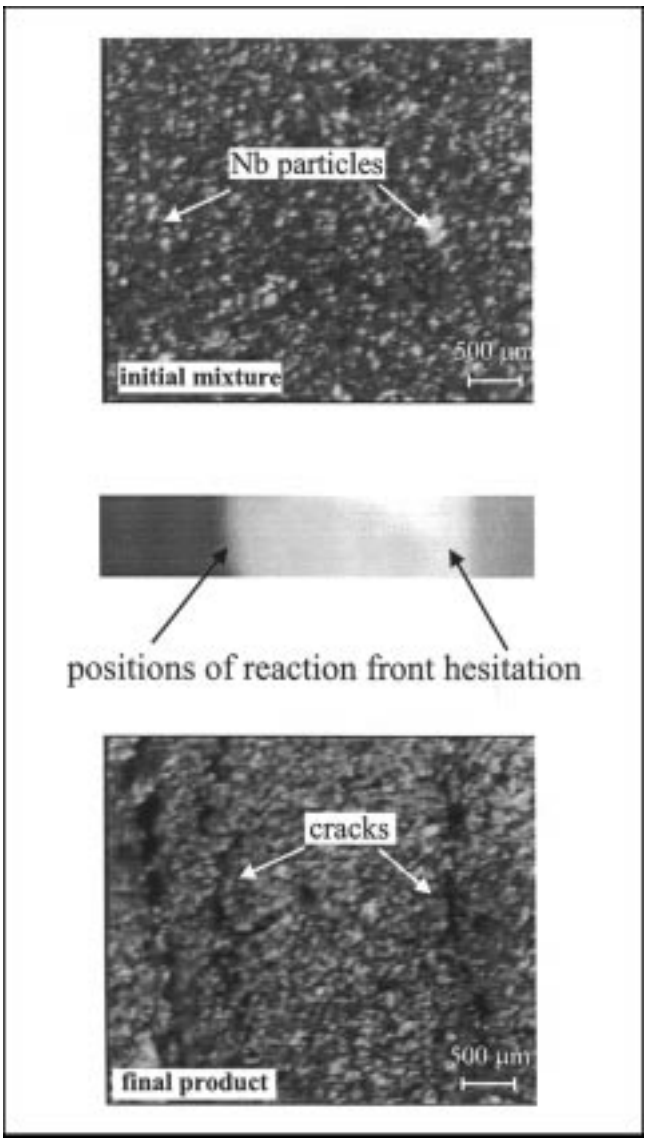

Figure 5. Micro pictures of the reaction medium, before and after combustion, in the Nb-B system.

Similar behavior was observed during combustion in the Ta + C system. As it can be seen from Figure 4b, when the crack forms, separate particle conglomerates are rapidly ejected from the crack, indicating the presence of local gas flux. This supports our hypothesis about the role of impurity gas phase in crack-induced oscillations.

System Ti + xC

Another type of oscillation was observed during combustion in the Ti + C system. Dynamics of the combustion front motion and DHSMVR frames for the front propagation in Ti + xC mixture are presented in Figures 6 and 7, respectively. Several significant differences as compared to the Nb + B and Ta + C systems can be outlined for the case $x = 0.4$ ($\Delta H_f = 90$ kJ/mol). First, the stable propagation period is shorter and the distance of propagation between hesitations is smaller (~ 0.2 mm), while average reaction front velocity during this period is higher (15–20 cm/s). Secondly, the instantaneous combustion velocity decreases before the front stops. Also, hesitation periods (~ 50–100 ms) are much longer than periods of propagation (~ 10 ms). Finally, no cracks were observed during the combustion wave propagation in this system.

Summarizing all these features, we may classify the observed phenomenon as a sequence of ignition and extinction, and refer to it as *ignition-extinction oscillation*. In this regime, while propagating across some preheated layer, the reaction extinguishes, since the heat of reaction is not sufficient to sustain its further movement. During the hesitation period, the next layer of reactant mixture is preheated, leading eventually to its self-ignition. Increasing the specific heat of reaction, that is, using composition closer to stoichiometry (such as Ti + 0.6C; $\Delta H_f = 140$ kJ/mol), we observe shorter and more irregular periods of hesitations (see Figure 6, curve 2). It is interesting that the oscillations persist even for the full stoichiometric mixture ($x = 1$). However, in this case, they become random and can be observed only on length scale of reactant particles (~ 50 μm) and time scale $\sim 10^{-3}$–10^{-4} s. Note that this *scintillation reaction wave* regime of combustion wave propagation has been described elsewhere (Varma et al., 1998b).

Discussion

The systems Nb + B and Ta + C are commonly recognized as ''classical'' gasless systems exhibiting pulsating combustion (cf. Borovinskaya et al., 1974; Shkiro and Nersisyan, 1978). Based on experimental results obtained for these systems, the theoretical models of pulsating solid-phase combustion were developed (cf. Matkowsky and Sivashinsky, 1978; Aldushin et al., 1973). However, it is important to note that all prior experimental data have mainly macroscopic character (such as average combustion velocity and frequency of oscillations), while the theoretical results describe behavior of the combus-

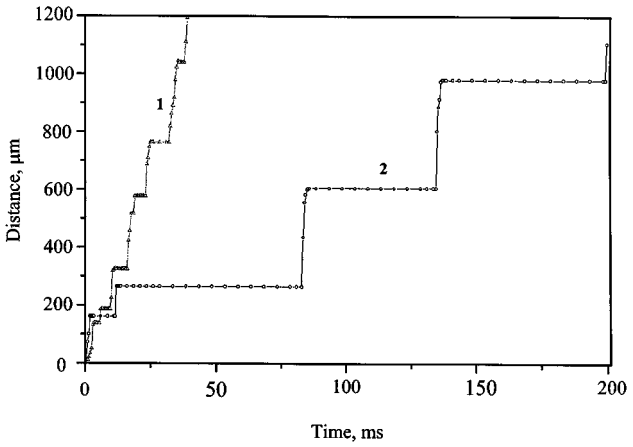

Figure 6. Characteristic dependencies of the reaction front location as a function of time in Ti + xC system ($\rho = 0.56$).

1: x = 0.6; 2: x = 0.4.

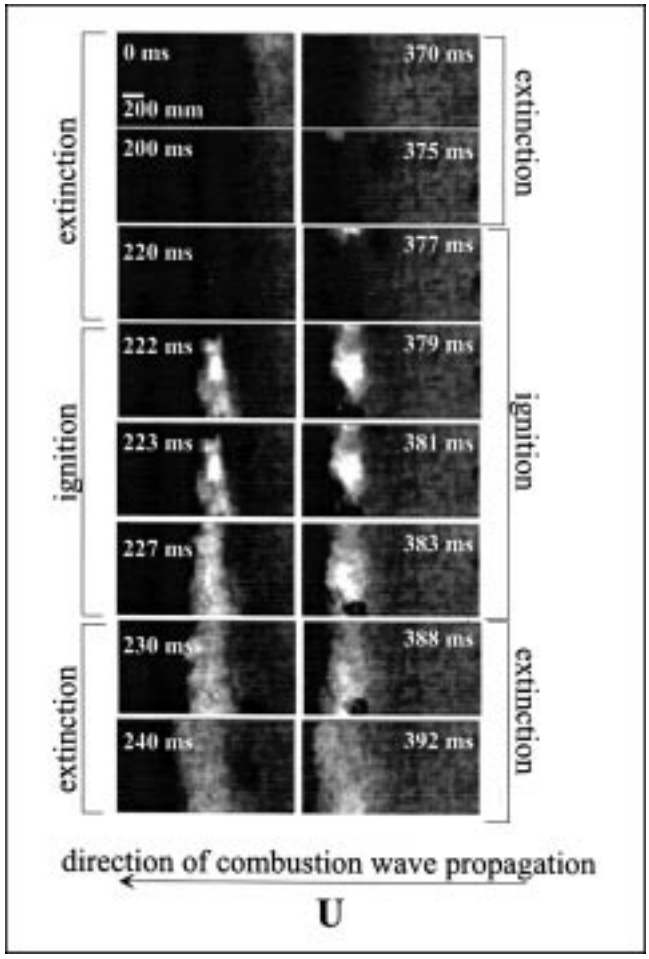

Figure 7. Sequences of video images illustrating microstructures of combustion wave in Ti + 0.4C system ($\rho = 0.56$).

tion wave at the microscopic level (such as instant combustion velocity, local temperature profile, and so on). The experimental data presented in this article quantitatively describe, for the first time, oscillations of local instantaneous velocity at the same length and time scales as considered by the existing theory of pulsating combustion. As discussed below, it appears that the experimental results cannot be described by existing theory.

The theoretical models are generally based on the assumption that pulsation is a result of thermal instability of steady-state combustion front propagation. Various stability criteria for steady wave propagation have been developed, and have the following typical form (cf. Shkadinskii et al., 1971)

$$\alpha = \left(9.1\frac{T_c}{T_c - T_0} - 2.5\right)\frac{RT_c}{E} \qquad (1)$$

where T_c is the adiabatic combustion temperature, R is the universal gas constant, E is the activation energy, and T_0 is the initial temperature of the reaction mixture. The boundary separating the steady and oscillating combustion modes is given by the conditions

$$\alpha > 1, \text{ stable steady state combustion,}$$
$$\alpha < 1, \text{ oscillatory combustion.} \qquad (2)$$

As may be seen from Eq. 1, decreasing T_c results in decreasing α, which may lead to pulsation. The theory also predicts that relatively small periodic oscillations of the combustion velocity should appear when α becomes slightly less than 1, with the amplitude of these oscillations increasing continuously with decreasing α. Finally, as α approaches ~ 0.8, the combustion velocity decreases gradually before the propagation extinguishes.

Examination of the experimental data obtained for Nb + B and Ta + C systems (Figures 3 and 4) leads us to the conclusion that observed oscillations of the combustion front propagation have different nature as compared with oscillations described by the theory. The experiments unequivocally show that the cause of oscillations is microstructural (crack appearance) rather than thermal. This proves the hypothesis made in early work that disruption of the medium continuity (fracture) may play a significant role in combustion front propagation (Merzhanov et al., 1973). It is apparent that every heterogeneous reaction medium has some critical mechanical stress which it can withstand. If a stress above this value occurs in the reaction front, one can expect that the medium will break up (that is, the crack will appear). The cause of such high internal stress is gas pressure in the pores, which arises due to desorption of impurity gases from the powder surface at the high temperature in the reaction front. Since the combustion velocity increases before hesitations (see Figure 3), we may expect that combustion of these systems could be stable if crack formation were prevented. Indeed, for Nb + B samples constrained to prevent lamination of the product, we observed stable combustion (see also Filonenko, 1975).

The oscillations observed in the Ti + xC mixture (Figures 6 and 7) have nature similar to the thermal oscillations described by theory. However, some important differences exist. As noted above, periods of propagation are much shorter than periods of stagnation, and propagating velocity is very high. This pattern better fits the process of ignition in the thermal explosion mode (see Merzhanov and Khaikin, 1988), rather than oscillations of propagating combustion wave.

In this case, the reacted part of the sample (product) plays the role of the hot wall contacted with the reaction mixture. After some induction period (observed as hesitation of the front), self-ignition occurs near this wall. Due to random distribution of the reactant particles, which cause local variations of physicochemical properties of the reaction medium, ignition occurs locally as hot spots and then rapidly propagates along the boundary between initial mixture and products (see Figure 7). However, combustion cannot propagate far ahead into the cold mixture because of limited heat evolution, and, hence, extinction occurs immediately after the thin preheated layer reacts fully.

It is interesting to note that thickness of the reacted layer is about several diameters of titanium particle. Therefore, thermal resistance of contacts between particles should be taken into account. It was shown in our previous work (Varma et al., 1998b) that the combustion front in Ti + C mixture

propagates due to a series of microscopic thermal explosions, each involving one reaction cell (that is, titanium particle surrounded by stoichiometric amount of carbon). Based on this mechanism, we may expect that macroscopic oscillations appear when the reacted cell cannot immediately ignite its neighboring unreacted cell, and heat spreads slowly preheating group of several subsequent particles. Thus, microscopic heterogeneity of the mixture must be considered as an important factor in pulsating combustion of gasless systems. The experimental results presented in this article provide the basis for further development of the theory of oscillating combustion.

Acknowledgments

This work was supported by the National Science Foundation (grants CTS-9528941 and CTS-9900357). We are also grateful to the Office of Research, University of Notre Dame, for cost-share funds.

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Manuscript received Apr. 28, 1999, and revision received July 28, 1999.