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# Flame propagation in a composite solid energetic material

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ABSTRACT

There is a growing interest in developing the micro and nanosized systems supporting the propagation of reaction waves for the needs of micropower generation and propulsion. Here we consider a thermal–diffusional model for composite energetic materials of the shell-core type which describes the propagation of combustion waves in such media of both nano and macroscopic sizes. It is demonstrated that by proper material design it is possible to substantially enhance the rate of combustion waves propagation and their stability. For macroscopic systems this opens possibilities for synthesis of new materials and creating new types of propulsion systems. For nanoscale systems we have found that the model substantially underpredicts the propagation velocities obtained in experiments thus implying that there are alternative ways for thermal energy transfer on such scales requiring further investigation.


## 1. Introduction

In a number of papers recently the possibility of developing of nanostructured composite energetic materials is discussed [1–7] in pursue for microscale power units with high energy density for microthrust and micropower generation applications such as micro–electro-mechanical systems including micropropulsion. The main idea behind this is in attempt to use the extraordinary material properties of nanostructures, which are not encountered in bulk materials, in order to modify and/or enhance the combustion characteristics of the resulting energetic materials. In [1–7] the composite consisting of an array of carbon nanotubes and combustible solids such as cyclotrimethylene trinitramine (TNA) is considered. Here we are mainly focused on the latter system. The basic building block of such material is a shell-core nanowire which has a carbon nanotube (CNT) in its centre and is covered with a shell of energetic material (TNA). Schematically this is illustrated in Fig. 1. It is reported [6] that such systems manifest unusual properties, for example, reaction wave speed can be orders of magnitude higher as compared to the bulk TNA due to the very high thermal conductance of CNT. Various applications of these materials are proposed such as microthrust and power generation. The latter is based on the Seebeck or thermoelectric effect [8]. It is known that CNT do not possess a high Seeback coefficient and probably are not the best candidates for micropower generation [9]. On the other hand to date a great number of nanowire (NW) arrays have been reported with various sizes and thermal and electrical properties [5]. Therefore there is a certain need to investigate these systems in a more general terms.

In [6,4] an attempt is made to describe the properties of the composite energetic material in terms of the well known thermal–diffusional models [10]. Leaving aside the issues of applicability of the diffusional heat transport on the scales of the several nanometres [9,11,12], as in the case of single wall CNT, and taking into account that different NW with much larger cross-sectional dimensions can be used, the same approach will be adopted in this current paper. The consideration will be focused on the fundamental one-dimensional formulation of the problem, which is obviously applicable on larger scales as well. In the latter case the problem is interesting from point of view of reaction wave synthesis applications such as self-propagating high temperature synthesis or for propulsion applications [13,14].

The multi-dimensional structures in the course of the flame propagation appear typically if the transverse thickness of a sample is larger than $c \cdot \mathcal{D}_T/S_L$, where $\mathcal{D}_T$ and $S_L$ are the thermal diffusivity and the velocity of the planar flame, respectively, and constant $c$ is typically $O(1)$ in the solid phase combustion. This situation is studied in [15–17] for cylindrical samples and in [14] for the model of hollow shell made of energetic material with adiabatic inner and outer boundaries and shell thickness exceeding the thermal flame scale. In the present paper we consider the cases of thin samples of width significantly smaller than $\mathcal{D}_T/S_L$. This length scale can be estimated for the system TNA-CNT to be of the order of several

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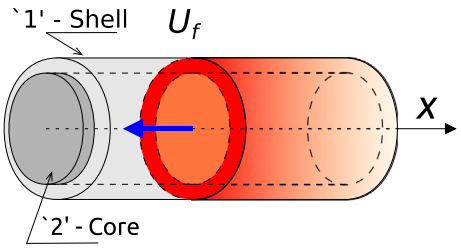


**Fig. 1.** Schematic diagram representing the propagation of the reaction wave in a shell–core composite material.

hundred microns. Therefore for the thickness of the energetic shell less then this scale the 2D and 3D structures are unlikely to appear and the one-dimensional approximation is feasible.

The kinetics of combustion reaction of energetic shell is described with a single irreversible step, whereas the NW/CNT core is considered to be an inert thermal conduit. This model is similar to some extend to the two-step competing reaction models [18] with the difference that the second reaction 'rate' is linear in temperature. Also depending on the difference of temperature of core and shell it can both absorb and provide heat to the reacting material. Therefore such system can possess a recuperation of heat similarly to combustion in microchannels [19] and one can expect an interesting stability properties of such flames. To the best of our knowledge stability of combustion waves in such systems has not been investigated previously.

## 2. General formulation

In order to describe the flame propagation a reference frame attached to the flame is used. Following the temperature distribution along the energetic material, $T_1$, starting from the unburned side, we choose a point $x = x_*$ (the first point if there are more than one) where the temperature is equal to some value $T_1 = T_*$. In the following, the reference frame is attached to this point. The chemical reaction is modelled by an over-all reaction step that converts a solid fuel to products at a mass rate proportional to $Y$ with Arrhenius temperature dependence $\Omega = \mathcal{B}Y\exp(-E/RT_1)$, where $T_1$ is the temperature and $Y$ is the mass fraction of the energetic material, $E$ is the activation energy of the reaction, while $\mathcal{B}$ represents the frequency factor of the reaction. The boundary conditions on the outer interface of the energetic material are considered to be adiabatic. In most cases these conditions are not exactly adiabatic, since there always exist conductive and/or radiative heat losses. Nevertheless the use of the adiabatic conditions is common in the literature in order to eliminate additional parameters and such approach can be justified if the characteristic time of the heat exchange with air is larger then the characteristic time of the flame propagation $\sim \mathcal{D}_T/S_L^2$. The study where these simplifications are relaxed is in progress.

We also can consider an array of closely packed shell-core structures (as it is done in experiments in [6]). In this case the heat is lost from the outer surface of the array and is therefore substantially reduced for each of the shell-core structures.

The dimensional balance equations describing conservations of energy in both mediums and mass of fuel take the form

$$S_1\left\{\rho_1 c_1\frac{\partial T_1}{\partial t}+\rho_1 c_1 U_f\frac{\partial T_1}{\partial x}-\lambda_1\frac{\partial^2 T_1}{\partial x^2}-Q\Omega\right\}=-PK(T_1-T_2), \quad (1)$$

$$S_2\left\{\rho_2 c_2\frac{\partial T_2}{\partial t}+\rho_2 c_2 U_f\frac{\partial T_2}{\partial x}-\lambda_2\frac{\partial^2 T_2}{\partial x^2}\right\}=PK(T_1-T_2), \quad (2)$$

$$S_1\left\{\rho_1\frac{\partial Y}{\partial t}+\rho_1 U_f\frac{\partial Y}{\partial x}-\Omega\right\}=0, \quad (3)$$

where indexes '1' and '2' refer to the solid combustible and pure conductive sections, $\rho_{1,2}$ is the density, $c_{1,2}$ is the specific heat, $T_{1,2}$ is the temperature, $\lambda_{1,2}$ - thermal conductivity, $S_{1,2}$ is the area of corresponding sections; $P$ is the perimeter of the intermediate surface, $K$ is an effective heat-exchange coefficient, $Q$ is the heat of the reaction. The value of the reaction wave velocity, $U_f$, is determines by the condition

$$T_1(x_*,t)=T_* \quad (4)$$

If the power generation is considered then one has to include additional terms in the energy balance equations corresponding to conversion of heat into electric current. However, as a rule, the efficiency of such conversion is quite low and more importantly, in this paper we are only interested in the flame propagation issues, therefore we do not take this into consideration.

The mass fraction is normalised with respect to the upstream value, $Y_0$, and non-dimensional temperatures, $\theta_1=(T_1-T_0)/(T_a-T_0)$ and $\theta_2=(T_2-T_0)/(T_a-T_0)$, are introduced where $T_a=T_0+QY_0/c_1$ denotes the adiabatic flame temperature and $T_0$ is the ambient temperature. Let us define the characteristic time and length using the relations

$$t_c=\beta\mathcal{B}^{-1}\exp(E/RT_a),\quad l_c=\sqrt{t_c\alpha_1}, \quad (5)$$

where $\beta=\gamma E/RT_a$ is the Zel'dovich number and $\gamma=(T_a-T_0)/T_a$ is the heat release parameter. The non-dimensional governing equations become

$$\frac{\partial\theta_1}{\partial t}+u_f\frac{\partial\theta_1}{\partial x}=\frac{\partial^2\theta_1}{\partial x^2}+\omega-\xi\cdot(\theta_1-\theta_2), \quad (6)$$

$$\frac{\partial\theta_2}{\partial t}+u_f\frac{\partial\theta_2}{\partial x}=\alpha\frac{\partial^2\theta_2}{\partial x^2}+s\cdot\xi\cdot(\theta_1-\theta_2), \quad (7)$$

$$\frac{\partial Y}{\partial t}+u_f\frac{\partial Y}{\partial x}=-\omega \quad (8)$$

with $u_f=t_cU_f/l_c$ representing the dimensionless flame velocity and the dimensionless reaction rate $\omega$ given by

$$\omega=\beta Y\exp\left\{\frac{\beta(\theta_1-1)}{1+\gamma(\theta_1-1)}\right\}. \quad (9)$$

Appropriate boundary conditions corresponding the configuration depicted in Fig. 1 are

$$\begin{aligned} &x\to-\infty: \quad \theta_1=\theta_2=Y-1=0,\\ &x\to+\infty: \quad \partial Y/\partial x=\partial\theta_1/\partial x=\partial\theta_2/\partial x=0 \end{aligned} \quad (10)$$

far upstream and downstream.

The geometric parameters appearing in these equations are

$$\xi=\frac{KP\beta\exp(E/RT_a)}{\rho_1 c_1 S_1\mathcal{B}},\quad s=\frac{\rho_1 c_1 S_1}{\rho_2 c_2 S_2}. \quad (11)$$

The last parameter can be easily changed in experiments. The parameter $\alpha=\alpha_2/\alpha_1$ gives the ratio of the thermal diffusivities $\alpha_1=\lambda_1/\rho_1 c_1$ and $\alpha_2=\lambda_2/\rho_2 c_2$. The case $\xi=0$ describes to the flame propagating in a pure energetic material neglecting the thermal exchange with the conductive supplement. The factor $\beta$ appearing in Eq. (9) provides that $u_f\to 1$ at $\beta\gg 1$ for $\xi=0$ in the case of the steady flame propagation.

In order to proceed with the analysis it is important to have in mind at least certain estimates for the ranges of variation of the parameters of the problem in Eqs. (6)–(10). For TNA-CNT system considered in [6] the Zel'dovich number vary from 5 to 14, whereas parameter $\alpha$ can reach the values as high as $10^4$. Parameter $s$ is mostly governed by geometric factors and taking the density and specific heat of TNA and CNT from [6,9] it can be evaluated as $s\sim 2.5\cdot S_1/S_2$. The ratio of cross sections of the energetic material and CNT core can be of the order of one for very thin shell or much higher depending on preparation process of the shell-core