Model of reduced kinetics for describing heterogeneous detonation in gas particle mixtures with non-uniform concentration distribution

T A Khmel and S I Tolkacheva

1Khristianovich Institute of Theoretical and Applied Mechanics SD RAS, 4/1 Institutskaya Street, 630090, Novosibirsk, Russia
2Novosibirsk State Technical University, 50 Marks Avenue, 630073, Novosibirsk, Russia

E-mail: khmel@itam.nsc.ru

Abstract. A simple model of reduced kinetics is proposed to describe the detonation combustion of gas particle suspensions with a non-uniform concentration distribution. The model is verified on the basis of empirical data on the dependence of the detonation velocity on the particle loading. The model constants for the substoichiometric and superstoichiometric suspensions of aluminum particles in oxygen are determined. The formation of suboxides and incomplete combustion of aluminum are taken into account integrally. Examples of numerical simulation of the Chapman-Jouguet detonation propagation in mixtures with longitudinal concentration gradients and cellular detonation in lean and superstoichiometric mixtures of aluminum and oxygen are presented.

1. Introduction

The study of the explosive characteristics of powders of reacting particles is of interest from the point of view of the safety of their use. Moreover, the addition of fine particles (boron, aluminum, etc.) to combustible gas mixtures increases their reactivity when used in jet propulsion devices, including detonation engines. A theoretical study of detonation of powder suspensions is based on experimental data. For a number of powders, experimental dependences of the detonation velocity on the initial loading of particles are known [1-2], which indicates a different degree of detonation combustion at different particle concentrations. This property is also noted for suspended particles of aluminum [3]. Aluminum powders are widely used in industrial technologies, and ultrafine aluminum particles represent great prospects for the use in composite fuels in devices based on detonation combustion. Therefore, it is relevant to analyze the conditions of ignition and combustion [4], as well as the characteristics of the modes of detonation of aluminum gas suspensions [5]. Numerical simulation of heterogeneous detonation flows is carried out mainly using the models of reduced kinetics of particle combustion. In [6], a semi-empirical model of heterogeneous detonation of micron suspensions of aluminum in oxygen was developed, verified according to experimental data [7] on the detonation velocity for stoichiometric composition. In [8], within the framework of the model, data on cellular detonation in aluminum gas suspensions were obtained. In [9-10], the model was generalized to a suspension of particles of the submicron and nanoscale range. Detonation of oxygen and air suspensions with concentrations other than stoichiometric ones was considered in [11–12]. Refined dependences of the detonation velocity on the concentration of particles in oxygen suspensions,
obtained on the basis of thermodynamic calculations of propagation of nonideal detonation in tubes, are given in [3].

This paper suggests a semi-empirical model of detonation combustion of aluminum particles in oxygen of arbitrary concentrations, verified according to [3] and describing detonation in non-uniform suspensions. The data of calculations of the propagation of detonation in gas suspensions of low (substoichiometric) or high (superstoichiometric) particle loading, as well as in media with longitudinal particle concentration gradients, are presented.

2. Physical and mathematical model

Two-dimensional detonation flows are described within the framework of the mechanics of interpenetrating continua by the Euler equations for the gas phase and particles. The system is closed by the equations of state and relations describing the interphase exchange of masses, momentum and energy.

\[
\frac{\partial \rho_i}{\partial t} + \frac{\partial \rho_i u_i}{\partial x} + \frac{\partial \rho_i v_i}{\partial y} = -(-1)^i J
\]

\[
\frac{\partial \rho_i u_i}{\partial t} + \frac{\partial \left[ \rho_i u_i (2-i) p / \rho_i \right]}{\partial x} + \frac{\partial \left[ \rho_i v_i (2-i) p / \rho_i \right]}{\partial y} = -(-1)^i (f_i - J u_i),
\]

\[
\frac{\partial \rho_i E_i}{\partial t} + \frac{\partial \rho_i u_i E_i + (2-i) p / \rho_i}{\partial x} + \frac{\partial \rho_i v_i E_i + (2-i) p / \rho_i}{\partial y} = -(-1)^i \left( q + f_i u_i + f_i v_i - J E_i \right),
\]

\[p = \rho_i R T_i, \quad E_i = u_i^2 / 2 + c_{i,i} T_i + (i-1) Q.\]

Here \( p \) is pressure, \( \rho_i, u_i, v_i, T_i, E_i, c_{i,i} \) are mean density, longitudinal and transversal velocity components, temperature, total energy per mass unit and heat capacity of the \( i \)-th phase (1, 2 indicate gas and particles, respectively). Mass concentrations of gas and particles are defined as \( \xi = \rho_i / \rho \), \( \rho = \sum \rho_i \), \( \rho_i = \rho_i m_i \), \( m_i \) is the volume concentration of the \( i \)-th phase.

Closure relations for the exchange of mass, momentum, and energy of micro- and nano-sized particles are presented in [8, 9, 10]. Particle combustion is described in the framework of the simplest model of one-stage kinetics, taking into account incomplete particle burning (the presence of residual concentration of unburned particles) and the regime of transition from diffusion-limited to kinetically-controlled combustion for particles with a diameter of less than 1 micron [4]. The dependence of the characteristic burning time of aluminum particles in the submicron range from 135 nm to 1 \( \mu \)m is taken as:

\[J = \frac{\rho}{\tau_{\xi}} (\xi - \xi_k) \exp(-E_a / RT_i) \text{ at } T_i \geq T_{ign}, \quad \xi > \xi_k \cdot J = 0 \text{ at } T_i < T_{ign} \text{ or } \xi \leq \xi_k.\]

\[\tau_{\xi} = \tau_0 \left( d / d_0 \right)^{-0.3} \exp\left( E_a / RT_i \right) \left( p / p_0 \right)^{-m} \]

where \( m = -0.25 \ln d[\mu m] \), \( E_a = 0.5 \E_{\text{micro}} (2 + \ln d[\mu m]) - \E_{\text{nano}} \ln d[\mu m] \), and \( \E_{\text{micro}} \) is the activation energy for micron particles (32 kJ/mol [4]), \( \E_{\text{nano}} \) is the activation energy for nanoparticles (60 kJ/mol [9, 10]), \( p \) is pressure, and \( d \) is the particle diameter.
For concentration-uniform suspensions of particles, the heat release of chemical reactions is constant and can be determined from empirical data on the normal (Chapman-Jouguet) detonation velocity. The oxidation of aluminum in an oxygen environment under conditions of detonation proceeds with the formation of both aluminum oxide $\text{Al}_2\text{O}_3$ and suboxides ($\text{AlO}$, $\text{Al}_2\text{O}_2$, $\text{Al}_2\text{O}_3$) [13], whose concentration in detonation products depends on the initial composition. Also, for the Chapman-Jouguet (CJ) normal detonation wave the propagation velocity depends on the initial composition [3]. In the framework of the simplest model of one-stage kinetics, the value of $Q$ includes the integral thermal effect of the particle combustion reaction, excluding the cost of heat for melting and evaporation of the particle material. According to experimental observations and data of thermodynamic calculations, the detonation velocity of gas particle suspensions depends on the initial concentration of particles (the stoichiometric composition of the mixture of aluminum and oxygen is about 1.6 km/s). The CJ velocity in numerical calculations is determined in the problem of the propagation of a planar detonation front in conjugation with a rarefaction wave. Also, the CJ velocity is an eigenvalue parameter in the problem of the structure of a stationary wave, which is reduced to solving a system of ordinary differential equations (ODE) resulting from (1) when moving to a coordinate system associated with the wave front. If this parameter corresponds to the CJ velocity in a two-phase mixture, the solution of an ODE system has either an internal sonic point (with respect to the frozen sound velocity) or a finite equilibrium state, which is sonic with respect to the equilibrium sound velocity [6]. In the pre-stoichiometric range, according to experimental data [7], it is assumed that $\xi_0 = 0.1$. The corresponding values of the parameter $Q$ for particles with a diameter of 1 μm and different particle concentrations are presented in Table 1. For conditions of high loading (superstoichiometry), an additional determining parameter is the portion of unburnt particles $\xi_\infty$. Table 2 shows the calculated values of the residual concentration at $Q$ value corresponding to stoichiometry, which are well approximated by the function $\xi_\infty = 0.1\xi_0 + 3.3(\xi_0 - 0.55)(\xi_0 - 0.4)$, which tends to 1 with $\xi_0 \to 1$.

**Table 1.** Detonation velocity and calculated total heat release in aluminum-oxygen mixtures of substoichiometric compositions.

| $\zeta$ | $u_0$ | $Q$ |
|--------|-------|-----|
| 0.2    | 1.66  | 10.9|
| 0.3    | 1.69  | 7.7 |
| 0.4    | 1.67  | 5.7 |
| 0.5    | 1.61  | 4.2 |
| 0.55   | 1.59  | 3.7 |

**Table 2.** Detonation velocity and calculated concentrations of unburnt particles in aluminum-oxygen mixtures of superstoichiometric compositions.

| $\zeta$ | $u_0$ | $\xi_\infty$ |
|--------|-------|--------------|
| 0.2    | 1.66  | 10.9         |
| 0.55   | 1.59  | 0.055        |
| 0.58   | 1.56  | 0.0868       |
| 0.6    | 1.54  | 0.1081       |
| 0.63   | 1.52  | 0.1352       |
| 0.67   | 1.51  | 0.1516       |
| 0.7    | 1.48  | 0.1765       |
| 0.73   | 1.46  | 0.2028       |
| 0.75   | 1.36  | 0.2754       |
| 0.77   | 1.3   | 0.3132       |
In a non-uniform suspension, the initial concentration distribution is given by function $\xi(x,y)$. Accordingly, the thermal effect of the reaction and the proportion of unburned particles at each point in space are different and depend on what was the initial concentration of the volume of particles that arrived at this point in space. To do this, function $\zeta(x,y)$ is introduced as follows: the initial distribution corresponds to the concentration distribution $\xi_0(x,y) = \xi(x,y)$, and as the mixture moves, it is determined from the equation $D\zeta /Dt = 0$, which, taking into account (1), is equivalent to

$$\frac{\partial \rho u \zeta}{\partial t} + \frac{\partial \rho u \zeta}{\partial x} + \frac{\partial \rho \zeta^2}{\partial y} = -F\zeta$$

(3)

The parameters $Q(\zeta)$ and $\xi_k(\zeta)$ are defined by the functions determined from the approximation of the data of Table 1 and Table 2.

Below are the results of calculations of one-dimensional and two-dimensional flows during the initiation and propagation of a detonation wave in a flat channel. The numerical technique is based on the conservative flux-splitting schemes: the TVD scheme by Harten for gas and the Gentry-Martin-Daly scheme for particles. The numerical method has been tested earlier and applied for 2-D numerical simulations of the shock wave and detonation flows. The step of the finite-difference grid was determined according to the scale of the relaxation zones, varied in the test calculations.

3. Results of calculations

3.1. Propagation of a detonation wave in a mixture with concentration gradients

Examples of calculations of propagation of a plane detonation wave in suspensions with longitudinal concentration gradients (positive or negative) are presented in Fig. 1 in the form of profiles of the main flow parameters in the wave structure with a time step of 0.04 ms. The concentration distribution was set by linear functions: decreasing $\xi_0(x) = 0.55 − 0.3125x$ (solid lines in Fig. 1), increasing $\xi_k(x) = 0.3 + 0.3125x$ (dashed lines in Fig. 1). The locations of the jumps on the lines allow determining the propagation velocity. They indicate the acceleration of the front in a medium with a negative concentration gradient (solid lines). Accordingly, in a medium with a positive gradient of the initial concentration of particles, the propagation of the detonation front slows down (dashed lines). The detonation velocities correspond to the data [3] presented in Table 1. It can also be seen that the peak values of the density of particles in the $\rho$-layer vary significantly in accordance with the change in concentration. It can be noted that the peak values of gas parameters vary in different ways depending on the initial concentration. The maximal pressures and densities of the gas in the considered range of values $\xi_0$ (from 0.3 to 0.55) also increase (although not as significantly) with increasing peak values of the particle density. The maximal temperatures and gas velocities in the detonation wave, on the contrary, decrease with increasing $\xi_0$ in accordance with the decrease in the velocity of propagation of the front.
Figure 1. Flow parameters at detonation propagation in mixtures with longitudinal concentration gradients: negative (solid lines), positive (dashed lines), $\Delta t=0.04$ ms.

(a)

(b)

Figure 2. Cellular detonation in homogeneous aluminum – oxygen suspensions of different concentrations: $\xi_0=0.4$ (a); $\xi_0=0.75$ (b).

Figure 2 shows pictures of cellular detonation in homogeneous pre- and superstoichiometric suspensions. The flow pictures are constructed using single color scale. The color differences in Figs. 2 and 2b indicate significantly higher peak detonation pressures of cellular detonations in superstoichiometric mixtures. That is, the trend of increasing peak pressures with an increase in the initial loading of particles remains in 2-D calculations. The average propagation velocity of the detonation front in cellular detonation at $\xi_0=0.75$, $\xi_0=0.275$ in numerical calculations is approximately 1.37 km/s, which corresponds to the value of the solution of the problem of the stationary structure of the ODE system and data [3] (Table 2).

It can also be noted that despite the significant differences in gas parameters such as pressure and density in the wave structure with pre-stoichiometry and superstoichiometry, the sizes of detonation cells of microdispersed suspensions are close (only some irregularity is observed in Fig. 2a). A possible explanation for this fact is the following. As shown in the works on the simulation of
detonation in microdispersed stoichiometric suspensions of aluminum [8, 14], the main characteristic that determines the geometric dimensions of the cells is function \( \phi(x) = u_i^2 - c_j^2 \), where \( c_j^2 = \gamma RT_i \) is the frozen sound velocity in the mixture. Since, as it can be seen from Fig. 1, the gas velocity and gas temperature are even less dependent on the initial particle concentrations than the pressure (and much weaker than the particle density), then this also has a weak effect on the cell size. Analysis of cellular detonation of nonstoichiometric suspensions of nano-sized particles requires additional research, since irregular cellular structures were obtained for stoichiometric compositions, which are characterized by significantly higher values of peak pressures [15].

Conclusions
The paper proposes a method for constructing a simple model of reduced kinetics for describing the detonation combustion of gas particle suspensions with inhomogeneous concentration distribution. The model is verified on the basis of empirical data on the dependence of the detonation velocity on the particle loading. For gas mixtures of aluminum particles in oxygen, the model constants are determined, which ensured agreement with known data on the detonation velocity. For the pre-stoichiometric compositions, the oxidation of aluminum with the formation of suboxides in detonation products is taken into account, and the integral heat release of chemical reactions is determined. For superstoichiometric compositions, the proportion of unburned aluminum is calculated assuming constant heat release. Examples of numerical simulation of the Chapman-Jouguet detonation propagation in mixtures with longitudinal concentration gradients and cellular detonation in lean and superstoichiometric mixtures of aluminum and oxygen are presented. Numerical calculations confirm the increase in the velocity of propagation of detonation in the areas of stoichiometry and the slowing of the front in the zone of superstoichiometry. In cellular detonation of lean and superstoichiometric microdispersed suspensions, there are significant differences in mean and peak pressure values, while the sizes of detonation cells are comparable. The model, due to its simplicity, can be easily integrated into numerical algorithms when modeling complex detonation flows.

Acknowledgements
The research was funded by RFBR and NSFC according to the research project No. 18-58-53031.

References
[1] Edwards D H, Fearnley P J, Nettleton M A 1987 Comb., Explosion, and Shock Waves 23 239
[2] Kotomin A A, Dushenok S A, Ilyushin M A 2017 Comb., Explosion, and Shock Waves 53 353
[3] Veyssiere B, Khasainov B A, Briand A 2008 Shock Waves 18 307
[4] Sundaram D S, Yang V, Zarko V E 2015 Comb., Explosion, and Shock Waves 51 173
[5] Veyssiere B 2006 Journal of Propulsion and Power 22 1269
[6] Fedorov A V, Fomin V M, Khmel’ T A 1999 Shock Waves 9 313
[7] Strauss W A 1968 AIAA Journal 6 1753
[8] Fedorov A V, Khmel’ T A 2005 Comb., Explosion, and Shock Waves 41 435
[9] Fedorov A V, Khmel’ T A 2018 Comb., Explosion, and Shock Waves 54
[10] Fedorov A V, Khmel’ T A, Lavruk S A 2017 Journal of Physics: Conf. Series 894 012049
[11] Veyssiere B, Khasainov B 1991 Combustion and Flame 85 241
[12] Benkewicz K, Hayashi A K 2003 Shock Waves 13 385
[13] Vasil’ev V M, Vol’pert A I, Klychnikov L V, et al 1980 Comb., Explosion, and Shock Waves 16 355
[14] Fedorov A V, Khmel’ T A 2008 Comb., Explosion, and Shock Waves 44 343
[15] Khmel T A 2017 Journal of Physics: Conf. Series 894 012099