Cellular detonations in nano-sized aluminum particle gas suspensions

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Abstract. Formation of cellular detonation structures in monodisperse nano-sized aluminum particle – oxygen suspensions is studied by methods of numerical simulations of two-dimensional detonation flows. The detonation combustion are described within the semi-empirical model developed earlier which takes into account transition of the regime of aluminum particle combustion from diffusion to kinetic for micro-sized and nano-sized particles. The free-molecular effects are considered in the processes of heat and velocity relaxation of the phases. The specific features of the cellular detonation of nanoparticle suspensions comparing with micron-sized suspensions are irregular cellular structures, much higher pick pressure values, and relatively larger detonation cells. This is due to high value of activation energy of reduced chemical reaction of aluminum particle combustion in kinetic regime.

1. Introduction

The combustion of nano-dispersed aluminum powders, including in the detonation mode, attracts great interest in view of the wide prospects for their use. The problems of detonations in aluminum particles gas suspensions have been extensively studied experimentally and theoretically for the micro-dimensional particle size range.

There are several theoretical models of detonation of aluminum dust in air, detonation products of gaseous mixtures, and oxygen [1 - 3]. In [4, 5], a model of heterogeneous detonation of monodisperse gaseous suspensions of aluminum particles in oxygen with a particle diameter of 1-10 μm was developed. The model has been verified by experimental data [6] on detonation velocity. Also agreements with known experimental data on reaction zone length, initiation energy, and detonation cell size was obtained in calculations within the framework of the model. The data on the propagation of cellular detonations in planar channels in monodisperse and polydisperse suspensions were obtained in [7, 8] and analogous problems for volumes of changing geometry were considered in [9, 10, 11].

In recent years, interest in research in the field of nanodispersed media has increased. A comprehensive review of new experimental data on the ignition, melting, heat transfer, and combustion of submicron and nanoscale aluminum particles is given in [12].

In [14], using the experimental data [12, 13], a semi-empirical physical and mathematical model of detonation of nanoscale aluminum particles in oxygen was constructed. The model takes into account the free-molecular effects in the description of the flow around and heat transfer of nanoscale particles with gas. It is expressed in the dependence of the characteristic times of the velocity and temperature relaxation processes on the Knudsen number. The simplest analysis of stationary detonation structures
showed that in the nanoscale range of particle diameters the burning times are much longer (order of magnitude more for 100-nm particles) than the times of thermal and velocity relaxation. It means that the combustion proceeds essentially in equilibrium mixture with respect to the velocities and temperatures of the phases. In addition, the specific feature of nanoscale particles burning is the transition from the diffusion combustion regime inherent in micro-dimensional suspensions [2] to the kinetic regime [12], characterized by much higher values of the activation energy of the combustion reaction [15]. These properties bring nano-sized aluminum suspensions closer to gas mixtures. In this connection, it is of interest to what extent this will affect the characteristics of cellular detonation.

The purpose of this paper is to analyze cellular detonation in gas suspensions of nanoscale aluminum particles [13] we use the same data as in [7-11].

2. Physical and mathematical model

The Euler equations for two-dimensional flow in dilute gas particle suspensions follow from conservation laws for mass, momentum, and energy (the subscripts 1, 2 indicate gas and reactive particles, respectively):

\[
\begin{align*}
\frac{\partial W}{\partial t} + \frac{\partial F}{\partial x} + \frac{\partial G}{\partial y} &= \Gamma, \\
W &= \begin{pmatrix} W_1 \\ W_2 \end{pmatrix}, \\
F &= \begin{pmatrix} F_1 \\ F_2 \end{pmatrix}, \\
G &= \begin{pmatrix} G_1 \\ G_2 \end{pmatrix}, \\
\Gamma &= \begin{pmatrix} -\Gamma_2 \\ \Gamma_2 \end{pmatrix},
\end{align*}
\]

\[
\begin{align*}
W_1 &= \begin{pmatrix} \rho_1 \\ \rho_1 u_1 \\ \rho_1 v_1 \\ \rho_1 E_1 \end{pmatrix}, \\
F_1 &= \begin{pmatrix} \rho_1 u_1 \\ \rho_1 u_1^2 + p + \rho_1 u_1 v_1 \\ \rho_1 u_1 v_1 \\ \rho_1 u_1 E_1 + p u_1 \end{pmatrix}, \\
G_1 &= \begin{pmatrix} \rho_1 v_1 \\ p + \rho_1 v_1^2 \\ \rho_1 v_1 E_1 + p v_1 \end{pmatrix},
\end{align*}
\]

\[
W_2 = \begin{pmatrix} \rho_2 \\ \rho_2 u_2 \\ \rho_2 v_2 \\ \rho_2 E_2 \end{pmatrix}, \\
F_2 = \begin{pmatrix} \rho_2 u_2 \\ \rho_2 u_2^2 \\ \rho_2 u_2 v_2 \\ \rho_2 v_2 E_2 \end{pmatrix}, \\
G_2 = \begin{pmatrix} \rho_2 v_2 \\ \rho_2 u_2 v_2 \\ \rho_2 v_2^2 \\ \rho_2 v_2 E_2 \end{pmatrix}, \\
\Gamma_2 = \begin{pmatrix} -J \\ f_{2x} \\ f_{2y} \\ q_2 + f_{2x} u_2 + f_{2y} v_2 \end{pmatrix}.
\]

The system is enclosed by the equations of state and relationships for mass, momentum, and heat exchange between the gas and the particles

\[
\begin{align*}
\bar{\dot{f}} &= \frac{\rho_2}{\tau_u} (\bar{u}_1 - \bar{u}_2), \\
q &= \frac{\rho_2 c_{v2}^2}{\tau_T} (T_1 - T_2), \\
J &= \frac{\rho_2}{\tau_\xi} (\bar{\xi} - \bar{\xi}_e), \\
p &= \rho_R T_1, \\
E_1 &= c_{v1} T_1 + 0.5u_1^2, \\
E_2 &= c_{v2} T_2 + Q + 0.5u_2^2.
\end{align*}
\]

Here indexes 1 and 2 refer to gas and particle, respectively. We use the following notations: \( p \) is pressure; \( \rho = m_0 \rho_u, u_i, E_i, T_i, c_{v,i}, m_i \), are mean densities, velocities, total energy per unit mass, temperatures, heat capacities, and volume concentrations of the components, \( \bar{\xi} = \rho_2 / \rho \) is mass particle concentration, \( \bar{\xi}_e \) is fraction of unburnt particles, \( \rho_u \) are true densities, \( R \) is the reduced gas constant, \( Q \) is heat effect of particle combustion in the frame of reduced chemical kinetics. The value of \( Q \) has been determined to agree with experimental data by Strauss [6] on detonation velocity. Since weak dependence of detonation velocity on particle diameter for micro-sized and nano-sized aluminum particles [13] we use the same data as in [7-11].
The interphase interactions are presented by parameters $J$ (the mass transfer), $f$ (the interphase interaction force), and $q$ (the heat transfer). The processes of velocity relaxation and heat transfer in gas-laden nanoscale particles are characterized by a transition from a continual to a free-molecular regime of particle interaction with gas molecules. If the particle size is comparable with the mean free path of gas molecules, then the particle drag force in the gas flow is determined with regard for the Cunningham correction factor [12]:

$$
\tau_u = 4d\rho_{s} C_c/3c_d\rho_1|\bar{u}_i - \bar{u}_s|, \quad C_c = 1 + 2Kn[1.257 + 0.4\exp(-1.1/2Kn)].
$$

Here $Kn = RT_i/(\sqrt{2\pi}d_p^2N_d\rho_d)$ is the Knudsen number that is the ratio of the mean free path of the molecular in gas to the particle diameter, $d_p$, $m_g$ are the gas molecular size and mass, $N_A$ is the Avogadro number. The drag coefficient $c_D$ is determined similar to micron-sized particle detonations with regard for supersonic flow around particle in detonation structure using the formula [7-11]

$$
c_D(Re, M_{12}) = \left(1 + \exp\left(-\frac{0.43}{M_{12}^{1.67}}\right)\right)\left(0.38 + \frac{24}{Re} + \frac{4}{\sqrt{Re}}\right),
$$

where $\mu_i$ is the gas dynamic viscosity and $\gamma_i$ is the adiabatic exponent.

The heat exchange between the gas and particles for submicron and nano-sized particles is determined following to changing the flow regime of particles from the continuum at Knudsen numbers below 0.01 to the free-molecular one at $Kn > 10$ [12]. Presentations for the characteristic times of heat relaxation in the regimes mentioned have a different form

$$
\tau_{T^{cont}} = d^2\rho_{s}C_{n/2}/6\lambda_i\text{Nu}, \quad \text{Nu} = 2 + 0.6Re^{1/3}Pr^{1/3},
$$

$$
\tau_{T^{fm}} = \frac{d^2\rho_{s}C_{n/2}}{6\alpha_p}\sqrt{\frac{8\pi m_g T_i}{k_b}}\left(\frac{\gamma_i - 1}{\gamma_i + 1}\right).
$$

Here Nu, Pr are the Nusselt and Prandtl numbers (usually, Pr=0.7), $\lambda_i$ is the gas heat conductivity, $k_B$ is the Boltzman constant, $\alpha$ is the accommodation coefficient. In the particle size range 10 nm - 1 μm, the Knudsen number varies from about 0.01 to about 10, respectively, the flow regime is transitional. For the transition region we suggest a logarithmic interpolation formula [14].

$$
\tau_{T^{fr}} = [(\log Kn + 2)\tau_{T^{fm}} + (1 - \log Kn)\tau_{T^{cont}}]/3.
$$

The processes of ignition and combustion of nanoscale aluminum particles are described using the known empirical data given in [12, 15]. A temperature criterion for the ignition of micron-sized particles with an ignition temperature of about 900 K (which is close to the melting point of Al) was adopted in works by A.V. Fedorov et al [7-11]. According to numerous experimental data on aluminum nanoparticle ignition presented in [12], we take for particles of size 50 ÷ 250 nm the ignition temperature equal to the melting point $T_{ign} = T_{melt} = 930$ K.

For describing the detonation combustion of a stoichiometric suspension of aluminum with dispersion 50 nm $\leq d \leq 250$ nm we assume the following approximation for the characteristic time of combustion in oxygen [12, 15, 14]
\[
\tau_\varepsilon = \tau_0 (d/d_0)^{0.3} \exp\left(\frac{E_a}{RT}\right)\left(\frac{p}{p_\ast}\right)^{-m}
\]  

(8)

with constants: \(d_0=80 \text{ nm}, \ p_\ast=8 \text{ atm}; \ E_a = 60 \text{ kJ/mol, } m = 0.5, \ \tau_0 =0.2 \mu s.\) For micron-sized and submicron suspensions we use the detonation model \([7]\) with activation energy of the Arrhenius type kinetics 32 kJ/mol (half the data for aluminum nanoparticles), thus reflecting the transitional combustion regime.

\[
\tau_\varepsilon = \tau_0 (d/d_0)^{0.3} \exp\left(\frac{E_a}{RT}\right)
\]  

(9)

with \(d_0=3.5 \mu m, \ E_a = 32 \text{ kJ/mol, } \tau_0 =0.294 \mu s.\) In the particle size range 50 nm - 250 nm, the values \(E_a, m\) and the relaxation parameters differ significantly from the data for the micrometer particles. A specific feature of the stationary detonation structures in nano-sized particle gas suspension is a significant difference in the scales of the relaxation zones (velocity and thermal) and the combustion zone. Also in a nano-sized suspension there is a significant difference in the scales of combustion zones of strong (over-compressed) and attenuated detonation waves due to large value of the activation energy. This may affect the characteristics of cellular detonations.

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 in \([7-11]\). The step of the finite-difference grid was determined according to the scale of the relaxation zones, varied in the test calculations. The calculations were performed using IBM PC Intel Core2Quad.

3. Formation of cellular detonation structures

We consider the problem of detonation initiation under interaction of a planar shock wave with a cloud of particles dispersed in a plane channel. A small perturbation of particle density on the cloud corner is posed to stimulate the transverse wave generations \([7]\).

Figures 1-5 present the maximal pressure history fields that reveal the trajectories of the triple points of cellular detonations. All the pictures in Figs. 1 - 5 are built in a single shadow scale. All the figures show that the system of transverse waves does not fold immediately, but after a while the propagation of detonation in the channel. Initially, weak transverse waves are amplified, traces of their collisions form cells. The geometric characteristics of the developed cellular structure depend on the particle size, the width of the channel, and also the parameters determining the extent of the combustion zone (in particular, the activation energy).

![Figure 1. The results of test calculations.](image_url)
Figures 1 show the results of test calculations for the suspension of particles with a diameter of 300 nm. In the fragments a) and b), the calculations were carried out without taking into account the Cunningham correct factor and dependence on the Knudsen number in heat exchange processes, the grid spacing was 0.0001 m (a) and 0.000075 m (b). The fragments c) and d) show the results, where these corrections were taken into account, the grid spacing is 0.000075 m (c) and 0.00005 m (d). As can be seen, for the suspensions of particles with diameters from 300 nm and higher, the free-molecular effects in the description of the flow around particle and heat transfer regime are insignificant. For calculations in the 300 - 600 nm range, the step was 0.000075 m, for particles of smaller diameters, the optimal step of the finite-difference grid was determined in similar way.

Figures 2 show examples of calculations for the suspension of 1-μm particles within the kinetics of micron-size particles (9) at $E_a = 32 \text{kJ/mol}$. As can be seen, the transverse waves formed from small perturbations are amplified as the front propagates, but the distances between them practically remain unchanged. It can also be noted that the trajectories of triple points are slightly different from straight lines and certainly smeared. The smearing character is due to the influence of relaxation zones comparable with the combustion zone of micron-size particles [5, 7]. The cell size correlates with the predictions of the acoustic theory [16], which is confirmed by calculations in [7]. The maximum pressures in the collision of triple points are of the order of 15 MPa, as was obtained in the calculations of [7].

Figures 3 show examples of calculations of cellular detonation formation in 1-cm channel for nano-sized gas suspensions of 100 nm (Fig. 3a) and 200 nm (Fig. 3b) particles obtained in the framework of the kinetic regime of aluminum combustion (8) at $E_a = 60 \text{kJ/mol}$. Here one can trace the similarities with the flow patterns of cellular gaseous detonation: the trajectories of triple points are much more clear-cut and more curved than in micron-sized suspensions (Fig. 2). It can also be noted that the initially formed system of transverse waves in the process of front propagation is significantly rearranged, the number of transverse waves decreases, the distance between them increases.
The effect of the channel width on the number of cells formed is shown in Fig. 4 on the example of calculation for a suspension of particles with a diameter of 600 nm. Here it can be seen that the irregularity of cellular structures takes place not only at the stage of cell formation, but also in the process of further propagation of detonation. Although the forming cell is much larger than at the initially formed transverse waves, they may then divide with subsequent re-establishing. The result of calculations in a rather wide channel (4-cm channel, $d=300$ nm) is shown in Fig. 5, where the irregularity of the cellular structure formed in the channel is more obvious.

Figure 4. Channel width effect on cellular detonations formation and propagation.

Figure 5. Evolution of the transverse waves.

Thus, in nano-dispersed aluminum-oxygen mixtures small-sized detonation cells are initially formed from small perturbations, and the distance between successive transverse waves agrees with the predictions of the acoustic theory [16, 7]. Further, as the front propagates and the transverse waves amplify, the cells are rearranged and enlarged. Trajectories of the triple points are highly curved, maximum pressures in the collision of transverse waves reach 40-50 MPa, which is three times higher than the values for micron-sized particles. Cellular structures are characterized by non-uniformity and irregularity. For micron-sized particles with a lower value of the activation energy of the reduced combustion kinetics (about 32 kJ/mol) [4], this behavior was not observed. From this it can be concluded that the properties listed above of cellular detonation of nano-dispersed mixtures are due to much higher values (60 kJ/mol) of the activation energy of the reduced kinetics of aluminum particle combustion.

4. Conclusions

Thus, nano-dispersed aluminum-oxygen mixtures small-sized detonation cells are initially formed from small perturbations, and the distance between successive transverse waves agrees with the predictions of the acoustic theory [16, 7]. Further, as the front propagates and the transverse waves amplify, the cells are rearranged and enlarged. Trajectories of the triple points are highly curved,
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Formation of cellular detonation structures in monodisperse nanosized aluminum particle – oxygen suspensions is studied by methods of numerical simulations of two-dimensional detonation flows.

The detonation combustion are described within the semiempirical model developed earlier which takes into account transition of the regime of aluminum particle combustion from diffusion to kinetic for micro-sized and nanosized particles. The free-molecular effects are considered in the processes of heat and velocity relaxation of the phases. It is established that for particles 300 nm and more coarse it is possible to neglect the free-molecular corrections in gas particle flow and heat transfer.

Common properties and specific features of the flows of suspensions of micro-sized or submicron particles and suspensions of nanoscale particles are established. The specific feature of the cellular detonation formation in nanoparticle suspensions is sufficient reconstruction of the primary weak transverse waves in the process of the detonation front propagation and their amplification.

The cellular detonation structures in developed detonation flow are irregular and characterized by much higher pick pressure values than in micro-disperse mixtures and relatively larger detonation cells. It seems that this is due to much higher value of activation energy of reduced chemical reaction of aluminum particle combustion in kinetic regime than in transition regime of combustion of micron-sized particles or diffusion regime of combustion of coarse aluminum particles.

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