Combustion of nano-sized aluminum particles in steam: Numerical modeling

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ABSTRACT

A model of the dynamics and mechanism of combustion of an ensemble of nanoscale aluminum particles in a steam is theoretically studied for adiabatic conditions. The formation of condensed phase is modeled for conditions when the homogeneous nucleation of gaseous Al_2O_3 species, processes of condensation/evaporation and coagulation of particles are taken into account. The model is used for studying the effects of the particle size, equivalence ratio, and chemical kinetics on the burning characteristics of aluminum-particle/steam mixtures. The calculated rate of combustion is limited by the rate of condensation growth of particles contained thermally unstable Al_2O_3 species. The details of the mechanism of interaction of the gas-phase reactions and the formation of particles are discussed. The results of numerical calculations are compared with experimental results of nano-aluminum dust combustion.

1. Introduction

Powdered metals (boron, magnesium, aluminum and others) as ingredients and the main components of engine fuels are successfully used for the rockets [1–4]. This explains the high number of publications devoted to the dynamics and mechanism of combustion of powdered aluminum [4–8] as well as others metals. The studies of preceding works are mainly focused on the combustion of aluminium particles with micron and larger sizes. In recent years, the nano-sized metal particles have increasingly come into scope of interest [9–12]. Attention to them is due to a number of properties that are unique for nano-sized metal particles. They are characterized by a lower melting point and ignition temperature in comparison with those for the micron sized particles; thus it seems possible to accelerate the combustion process when the nano-sized particles are used. In support of this assumption, the low-temperature ($\approx$1300–1500 K) ignition followed by rapid combustion ($\leq$1 ms) of nano-sized aluminum particles ($d = 38$ nm) (in the post-flame zone of hydrogen burned by oxygen) is reported [13]. The authors explain decrease of the ignition temperature by the heterogeneous chemical processes with gaseous oxidants (products of combustion of hydrogen/oxygen mixture) that is due to the negligibly low vapor pressure of aluminum at these temperatures. In contrary, the authors [14] conclude that combustion of the particles occurs mainly in the gas phase on the basis of experiments on the ignition and combustion of sub-micron Al particles

not covered by thin film of oxide in the gas mixture O_2–Ar. Due to higher reactivity of the particles the ignition temperature is in the range 500–600 K, i.e. below the melting point of Al. The particles are produced using Gen–Miller technique that is based on metal evaporation under an electromagnetic field and its subsequent condensation in the inert gas flow [15].

An important peculiarity of aluminum combustion is the formation of the condensed products (hereinafter c-phase) accompanied by releasing of a significant amount of heat ($\approx$50% of the total). The effect of the nucleation stage on the burning rate of micron sized aluminum particles is reported in [16]. The burning time of aluminum and water vapor premixed flame, we evaluated in previous work [17] where the condensation and coagulation of particles along with their nucleation are used for calculations. The time of combustion (t_{comb}) is assigned according to the following relationship: $(T_{comb} - T_0)/(T_{end} - T_0) = 0.95$ where T_{comb} is the temperature of the mixture at time t_{comb}; T_{end} is the thermodynamically equilibrated temperature of the mixture at the end of combustion, T_0 is the initial temperature. For example, the value of $t_{comb} \sim$ 10 ms is determined for $T_0 = 2700$ K. This result shows that the physical processes (formation of c-phase) occurred during combustion of homogeneous mixture can affect the flame velocity. This is in support of the results of experiments on combustion of nano-sized aluminum particles in air (Bunsen burner-type). The experiments show that the laminar flame velocity ($\sim$0.15 m/s, [11,18–19]) is not very different from that of micron-sized particles ($\sim$0.25 m/s, [20]). So, the purpose of this work is tracing of the detailed effect of processes of c-phase formation on the dynamics of combustion of an ensemble of nano-sized aluminum particles in steam flow.

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2. Statement of the problem

The problem of modeling of combustion of an ensemble of nano-sized aluminum particles in water vapor can be solved in the following formulation. At initial time $t = 0$, a preheated mixture of steam and monodisperse unoxidized aerosol particles of aluminum is introduced in the system. The evaporation of aluminum particles begins almost simultaneously with chemical gas-phase reactions as well as possible heterogeneous chemical reactions with aluminum particles. As a result, the formation of gaseous Al_2O_3 and its condensation in the form of fine particles (c-phase) takes place. Different signs of the thermal effects characterize each of these processes, including the phase transition.

There is a discussion about existing of gaseous Al_2O_3 due to its low thermal stability at high temperatures. The presence of the intermediate product is supported by photoelectron spectra of products of reaction of aluminum and oxygen atoms in the electric discharge plasma, as well as by the detection of $Al_2O_{3(g)}$ in matrix isolation and IR spectroscopy experiments [21–23]. The high concentration of aluminum suboxides in the combustion zone is obviously favorable for the formation of $Al_2O_{3(g)}$ molecules and their subsequent condensation on the aluminum oxide during the aluminum combustion. This is confirmed by presence of the tiny aluminum oxide particles outside of the aluminum droplets [24,25]. This does not exclude however the participation of aluminum suboxides in the formation of the condensed phase of $Al_2O_{3(c)}$, see, e.g., [26]. The role of these processes is apparently dominant during ignition of nano-aluminum particles at low temperatures ($\approx$1300–1500 K), that is observed, for example, in [13]. These processes also take place at high temperatures but as a first approximation, they are omitted to simplify the problem as well as other heterogeneous reactions.

The following statements are assumed in the model:

(a) the process is adiabatic and occurs under constant pressure (1 atm);
(b) the temperature distribution and concentration of components in the system is uniform at each time; no heat and mass transfer occurs between the elements of the system;
(c) a mixture of gaseous components is homogeneous all the time. This is true if the average distance between particles (X_{av}) and the mean path length of free motion of gas molecules (L_{av}) have the same order in value (for the calculations, it is assumed that $X_{av}/L_{av} < 10$);
(d) evaporation of aluminum from the surface of aerosol particles and its condensation on the aluminum oxide particles occurs in the kinetic regime (Knudsen number $Kn = L_{av}/r >> 1$, where r is the radius of the particles);
(e) formation of the aluminum oxide particles is due to condensation of the gaseous Al_2O_3;
(f) heterogeneous chemical reactions on the aluminum particles surface are neglected in the model.

The gas phase chemical transformations of the 16 individual components ($Al_{(c)}$, $Al_{(g)}$, $M_2O_{(g)}$, $M_{2(g)}$, $AlO_{(g)}$, $AlO_{2(g)}$, $AlOH_{(g)}$, $Al_2O_{(g)}$, $Al_2O_{2(g)}$, $AlH_{(g)}$, $M_{(g)}$, $O_{(g)}$, $OM_{(g)}$, $O_{2(g)}$, $Al_2O_{3(g)}$, and $Al_2O_{3(c)}$) are described by model with 46 kinetic equations. Here and below the indexes (g) and (c) indicate, respectively, the gas and condensed phases. A list of relevant chemical reactions is presented in Table 1. The rate constant for these reactions is presented in the form of modified Arrhenius equation:

$$K = AT^n \exp\left\{-\frac{Q}{T}\right\}, \tag{1}$$

where A is the pre-exponential factor; T is the temperature, K; n is a temperature power; $Q = E/R$ (where E is the activation energy of the reaction; and R is the gas constant).

The gas phase kinetic model (Table 1) must be completed by the following processes:

R47. $Al_{(c)} \rightleftarrows Al_{(g)}$ (2)

R48. $Al_2O_{3(g)} \rightleftarrows Al_2O_{3(c)}$ (3)

The rates of aluminum evaporation (R47) and Al_2O_3 condensation (R48) depend on the particle size, the composition of the gas mixture and its temperature. In case of Al_2O_3, the size distribution of formed particles is polydisperse.

The kinetic model of chemical transformations proposed in [27] is used with some amendments in the present paper, as well as in [20]. So, in the present work, the chain of subsequent slow reactions: $Al_{(g)} + H_2O_{(g)} \rightarrow AlOH_{(g)} + H_{(g)}$ and $AlOH_{(g)} + H_{(g)} \rightarrow AlO_{(g)} + H_{2(g)}$ is considered as the initiation of the combustion according to works [28,29], instead of the fast reaction $Al_{(g)} + H_2O_{(g)} \rightarrow AlO_{(g)} + H_{2(g)}$.

3. Evaporation of small particles and condensation on them

In the present work, the rates of evaporation of aluminum and condensation of aluminum oxide are calculated by taking into account temperature changes of nano-sized particles caused by these processes. The resulting interfacial exchange rate j (molecules per second, i.e. s^{-1}) for the component X presented simultaneously in the gas and condensed phases (a particle with radius r) is described by the following equation:

$$j = j_c(T) - j_v(T_s), \tag{4}$$

where $j_c(T)$ is the rate of condensation of vapor of the component X on the particle at the gas temperature T; $j_v(T_s)$ is the rate of its evaporation from the particle; T_s is the temperature of the particle.

The condensation of the component X on the particle occurs when $j > 0$, while its evaporation occurs at $j < 0$. If $T_s = T + \Delta T$, then in case of $|\Delta T/T| << 1$ the following equation can be derived:

$$j_v(T_s) = j_v(T) + \frac{\partial j_v}{\partial T}\Delta T \tag{5}$$

Let p be the vapor pressure of the component X in the gas mixture. The rate of vapor condensation j_c on the particle is equal to the number of molecules of the component X falling on the surface of the particle multiplied by the coefficient of condensation α_c. The rate of evaporation j_v from the surface of the particle is defined by taking into account its equality to the rate of condensation when the vapor pressure of the component X over the particle of radius r is in the equilibrium. Thus, the rates of evaporation and condensation in the kinetic mode at temperature T are:

$$j_v(T) = \frac{\alpha_c p_e^r \bar{V}S}{4kT}, \quad j_c(T) = \frac{\alpha_c p \bar{V}S}{4kT}, \tag{6}$$

where p_e^r is the equilibrium vapor pressure of the component X over the particle of radius r; $\bar{V}$ is the mean velocity of the molecules of the component X in the gas; and S is the surface area of the particle.

The equilibrium vapor pressure over the particle with radius r is given by the Thomson equation:

$$p_e^r = p_e \exp\left\{\frac{2\sigma v_c}{rkT}\right\}, \tag{7}$$

where p_e is the equilibrium vapor pressure of the component X over a flat surface; σ and $v_c = m/\rho$ are, respectively, the specific surface energy and the molecular volume of the component X in the condensed phase (m is the mass of the molecule, and ρ is the density of component X in the condensed phase).

In quasisteady-state conditions, the rate of heating/cooling of particle by condensation/evaporation is equal to the rate of heat exchange between surrounding gas and the particle of radius r (S is the