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SMOKY PLASMA IN A DUST FLAME

The results of experimental investigation of the influence of 0.1÷5.0 mass percent of K_2CO_3 and KCl additives on the dispersion of combustion products, which were obtained by the combustion of an Al gas suspension in a laminar diffusion flame, are presented. The extreme dependence between the average particle size of Al_2O_3 and the additive concentration (C_a) was experimentally observed. At the K_2CO_3 additive concentration over 0.5%, the increase in the average particle size of Al_2O_3 ($d_{10} \sim 50$ nm for $C_a = 5\%$) was observed. It is shown that a change in the character of dependence between the Al_2O_3 average particle size and the concentration of low ionizing additives is due to the interaction between the dust and the ion subsystems of the combustion product plasma in the flame combustion zone. The theoretical calculation of the ion concentration in the system, at which the ion drag force is comparable to the Coulomb force, was done.

Keywords: aluminum flame, gas-dispersion synthesis, low ionizing additives, combustion product dispersion, coagulation rate, dusty plasma.

1. Introduction

Today, there are many ways to get nano-sized metal oxide powders, among which is a special class, which has already become a classical one, of combustion methods. Of special interest is the method of gas-dispersion synthesis (GDS), which was developed at the Institute of Combustion and Advanced Technologies of I.I. Mechnikov Odessa National University. The main essence of this method is to burn a fine metal powder in a gaseous oxidizer. The most obvious advantages of this method is the high purity of target products – metal oxides, environmental friendliness, high productivity compared with other methods, and that the production of a metal oxide is a one-step process. If we consider the metal dust flame as a source of target products, the question about the possibilities of a deliberate action on the dispersion of synthesized products arises. The most obvious way to solve this problem is to vary the main parameters of the dust flame such as the concentration of fuel and oxidizer, the initial metal powder dispersion, the initial temperature of the reactants, *etc.* But, according to the results of previous studies [1], the variation of these parameters does not significantly affect the final product dispersion. The numerical calculations of the influence of the concentration of additives to the fuel on the metal oxide dispersion, which were made in [2], as well as experimental studies, whose results are presented in [3], have shown that an effective way to influence the target product size is to add low ionized substances to the metal powder. At the combustion of single metal particles and their gas suspensions in oxygen-containing environments, high temperatures reaching 1700–3500 K are produced [4]. The thermal gas phase ionization (nitrogen or other inert gases, oxygen) at such temperatures is negligible. The particles of the condensed phase suspended in a gas (the initial fuel, the condensed combustion products) get the positive charges as a result of the thermo– and photoemissions. The magnitude of charge depends on a material, size, and concentration of particles. The ionization equilibrium of the two-phase environment is significantly affected by the natural and specially introduced additives of low ionized atoms – atoms of the alkali metals or substances with high electron affinity. As a result, the condensed charged particles, electrons, and ions in the gas phase are formed in the combustion zone of the metal particle dust flame. The thermal ionization of a gas and condensed phases in the combustion zone is accompanied by the strong influence of electrical interactions on the rate of homogeneous nucleation of gaseous products of the metal combustion and increases the rate of ion-induced heterogeneous nucleation [5, 6]. Therefore, the kinetics of condensation in highly ionized environments may

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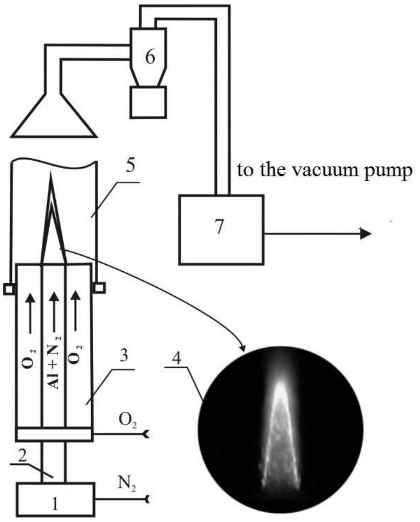

Fig. 1. Experimental setup: *1* – powder spraying unit; *2* – burner inner cylinder; *3* – burner outer cylinder; *4* – dust flame; *5* – moving tube to protect the flame; *6* – system for collecting the combustion products; *7* – fabric filter for collecting the combustion products

differ significantly from the condensation in electrically neutral systems. In particular, the barrier-free nucleation at low degrees of supersaturation of condensable vapors becomes possible [6]. Another important consequence of the ionization of the combustion zone is a decrease in the coagulation rate of electrically charged nuclei, since the contact between like-charged particles becomes impossible. It is obvious that, at a change of the ionization equilibrium conditions in the flame zone of combustion, the kinetics of nucleation and coagulation of the combustion gases and, therefore, the combustion product dispersed composition will be also changed.

The purpose of this work was to determine the effect of the concentration of a low-ionizing addition (potassium atoms) to aluminum on the dispersion and the phase composition of combustion products, which are produced at the gas-phase burning of the aluminum particle-gas suspension.

2. Experiment Technique

Previously, it was shown [1, 7] that nanoparticles of any metal pure oxides (Al_2O_3, Fe_2O_3, TiO_2, ZrO_2 and other) (particle average size – 40–100 nm) can be synthesized by the GDS. We can use metals, for which it is possible to get a self-sustaining two-phase flame, in which a metal powder is burned in a gaseous oxidizer. Aluminum powder with a particle average size of 4.8 microns was used as a fuel. Experiments were made with two kinds of low-ionizing additives: potassium carbonate (K_2CO_3) and potassium chloride (KCl). In the initial aluminum powder, a low-ionizing addition was added through an aqueous solution in amounts of 0.1, 0.5, 1.0 and 5.0% by mass. The suspension that was formed was dried, dispersed, and burned in a laminar diffusion two-phase flame (LDTF is a flame, in which the dispersed fuel in a inert gas burns in the co-flow stream of an oxidant). Methods of introduction of additives to a fuel were shown in details in [8]. The laboratory setup (Fig. 1) consists of three main blocks: dust burner, block of powder inning and spraying, and system of collecting combustion products. To investigate the mechanism of combustion of particles and a gas metal particle mixture and to determine the conditions of a self-sustaining flame stabilization, the setup includes devices for diagnostics, recording, control, and measurements. The burner consists of two coaxial stainless steel tubes, which are installed vertically. The fuel with inert gas (nitrogen) was supplied by inner coaxial tube (2); oxidizing gas of the necessary composition (usually, pure oxygen or a mixture of oxygen and nitrogen) by the outer tube. On the outer tube, another movable molybdenum glass tube (5) is fixed. It is used to protect the flame from external perturbations and allows us to carry out the visual observation, photo- and video-registration, and spectral studies. The dust-gas mixture was ignited once by the flame of a propane torch. The laminar self-sustaining flame was formed on the burner outlet by selecting the characteristics of the fuel and the oxidizer in the upper burner cut. The exterior view of a flame (4) is shown in Fig. 1. The formation of a combustion product plasma occurs in a narrow zone of the flame, which is called the combustion zone 1–2 mm in width. Aluminum oxide nanoparticles (Al_2O_3), which are captured by the filter at the upper base of the flame, are formed as a result of the aluminum particle-gas suspension combustion.

Then the samples of the combustion products were analyzed by a transmission electron microscope (TEM). Typical microphotographs of combustion products of aluminum with K_2CO_3 are presented in Fig. 2. It can be seen that, for powders with different contents of the additive, the form of particles is spherical in all cases. For samples with the KCl additive, the form of alumina particles was also spherical. For the photographs, which were obtained with a TEM, the disperse analysis was carried out, according to the method described in [9] in detail.

The phase composition of the Al_2O_3 samples was determined by the X-ray diffractometer XRD Rigaku. In all cases, the combustion product of aluminum with additives is aluminum oxide $\gamma - Al_2O_3$. The results of disperse analysis allowed us to plot a graph showing the dependence of the oxide particle average size on the concentration of the additive in the initial fuel (Fig. 3). It can be seen that the experimental dependence is extreme with strongly pronounced minimum.

3. Results and Discussion

A decrease in the characteristic particle size with increase in the concentration of potassium atoms was expected [1], and it is related to an increase in the concentration of K+ ions, which participate in the formation of product condensation centers of the vapor-phase or gas-phase combustion of aluminum. The calculation of the equilibrium combustion temperature showed that the increase in the addition content from 0 to 5% leads to the decrease in the combustion temperature only by 30 K from 3350 K to 3320 K. Therefore, it is improbable that the extremum appears due to a change of the combustion temperature at a variation of the addition concentration. The reason for the increase in the average size of Al_2O_3 particles with the concentration of a low-ionizing addition ($C_{K_2CO_3} > > 0.5\%$) can be, apparently, the interaction between electrically charged components of the strongly ionized two-phase environment in the combustion zone of a flame. It is known that a high temperature develops during the combustion of metal particles and their gas suspensions. This leads to the intense process of ionization of atoms and molecules with low ionization potential and to the thermionic emission from the surface of condensed particles. At the same time, the photoemission process can be neglected, because the free path of the radiation exceeds the characteristic system dimensions. In general, the system conserves the quasineutrality and may be considered as a plasma with condensed combustion products or dusty plasma. Dusty plasma properties are much more diverse than properties of a conventional multicomponent plasma of various types of electrons and ions. Dust particles are centers of the recombination of plasma electrons and ions, and they are the source of electrons due to different emission processes. Thus, the dust component can significantly affects the ionization equilibrium [10]. The introduction of an additive in a dusty plasma leads to a shift of the ionization balance. Indeed, at temperatures of about 3000 K developed in plasma of aluminum combustion products, atoms of an additive are ionized, by emitting electrons in the system and by changing their concentration. On the example of the K_2CO_3 additive, we shall consider the basic features of the ionization equilib-

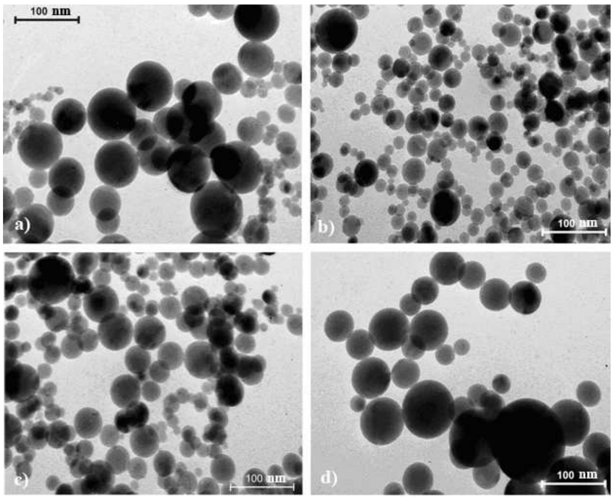

Fig. 2. Microphotographs of Al_2O_3 nanoparticles (magnification X 100 000): The concentration of an additive in the initial fuel contains: 0.1% K_2CO_3 (*a*); 0.5% K_2CO_3 (*b*); 1.0% K_2CO_3 (*c*); 5.0% K_2CO_3 (*d*)

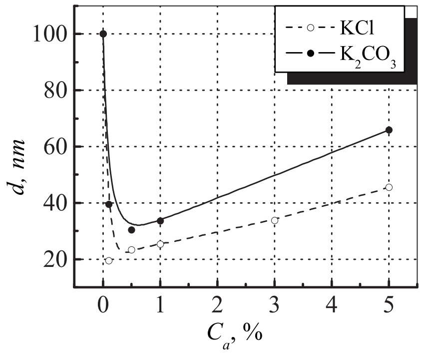

Fig. 3. Size of Al_2O_3 particles vs. the additive concentration in the initial fuel (points – experiment; dashed line is an approximation)

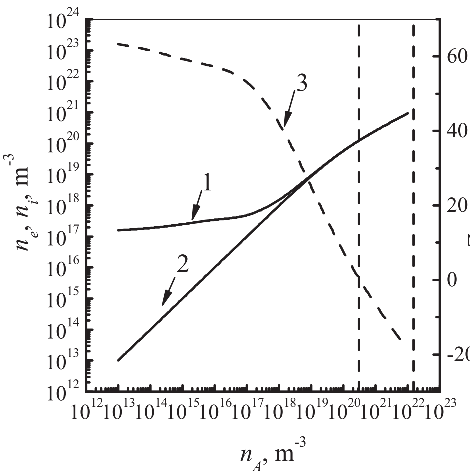

Fig. 4. Ionization equilibrium in the plasma of Al with K_2CO_3 additives; $C_{\rm Al} = 0.4$ kg/m^3 and $r_{30} =$ 50 nm. The vertical dashed lines mark the experimental region of the additive concentration; *1* — the concentration of electrons n_e, *2* — the concentration of ions, *3* — charge of the growing oxide nanoparticles Z

rium in the combustion zone of aluminum particles in the dusty flame. According to the calculation of system's ionization balance [8] for the additive concentration (potassium atoms) $n_{\rm A} < 10^{17}$ m^{-3}, the electron concentration is determined by the thermionic emission ($n_e \gg n_i$). In this case, the plasma in the combustion zone can be considered as a thermoemissive one, for which the electron density $n_e \approx Z_p n_p$.

At the further increase in the concentration of additive atoms $n_{\rm A}$, the ion concentration n_i becomes comparable to the concentration of electrons ($n_e \approx \approx n_i$). For concentrations of additive atoms ($n_{\rm A} > > 10^{18}$ m^{-3}), the particles of the condensed phase do not affect the ionization balance in the combustion zone of the flame. Under these conditions, the electron density n_e is determined not by their emission, but by the ionization of potassium atoms. When the concentration of electrons in the interparticle space becomes larger than the concentration of electrons near the surface of a particle, a flow of electrons to the surface of the particle appears, and, as a result, its charge changes a sign from positive to negative (Fig. 4, curve *3*). Here, $n_{\rm es} = 2\left(\frac{2\pi m_e kT}{h^2}\right)\exp\left(-\frac{W}{kT}\right)$ – the concentration of electrons on the surface of condensing particles, which is determined by Richardson equation, W – the work function of an electron from the Al_2O_3 particle surface ($W = 4.7$ eV), r_d — radius of oxide particles. The amount of negative charge increases with the concentration of additive atoms. It can be expected that the natural impurities, which are a part of aluminum in an amount of less than 10^{-4}–10^{-5}%, change not only the magnitude of a particle charge, but also its sign. However, the qualitative experiments with the aluminum particle flame placed in the constant electric field of a plate capacitor showed that the alumina particles are deposited on the negatively charged plate, i.e., have a positive charge. The results of calculations of the ionization equilibrium were used for the analysis of the coagulation of like-charged particles in the combustion zone at the growth of condensed phase particles. The temperature of Al_2O_3 particles in the combustion zone of the flame ($T_k \approx T_g = 3150$ K) is much greater than the melting point of Al_2O_3 ($T_m \sim 2400$ K). Hence, the collision of Al_2O_3 drops results in their fusion (coagulation), and a spherical drop of alumina with larger size is formed. The electric charge of the particle has an effect on the coagulation rate and usually leads to the completion of this step of condensation of gaseous combustion products. The expression for the coagulation rate of like-charged particles can be written in the form $\frac{k}{k_0} = \exp\left(-\frac{U_{\rm es}}{kt}\right)$, where $U_{\rm es}$ — energy of the electrostatic interaction of the charged particles, T – the temperature of environment. In Fig. 4, the dependence between the relative coagulation rate $(\frac{k}{k_0})$ and the concentration of potassium atoms is shown. From this dependence, it follows that, for the like-charged monodisperse Al_2O_3 particles, the particle charge prevents their contacts, and the coagulation of charged particles becomes impossible (curve 1). Thus, in the range of additive atom concentrations between the two vertical dashed lines in Fig. 5, the coagulation rate of particles decreases sharply, which should lead to an increase in the dispersity of the particles of combustion products. However, the inverse relationship is experimentally observed (see Fig. 3).

To explain the qualitative difference between the calculated and experimental results, it was suggested that, at sufficiently high concentrations of additives with the electrostatic repulsion of like-charged particles of the condensed phase, other forms of interaction between the components of the plasma begin to compete. As a result, this leads to the attraction of like-charged particles, thus contributing to an increase in the coagulation rate. The possibility of the attraction of like-charged particles is known in plasma physics. Possible mechanisms are the Le Sage's shadow forces, collective effects in plasma [12], polarization interaction of dust particles [11], and others. The analysis of the above mechanisms of interaction showed [8] that, for the nano-sized particles, the polarization mechanism of interaction is the most appropriate. The basic idea of the polarization model consists in the following: the particle placed in an electric field, which is created by the neighboring negatively charged macroparticle, is polarized. In turn, this leads to a redistribution of the ion flow along its surface. In this case, the additional force defined by the plasma flow (ion drag force or ionic wind) acts on the dust particle in an external electric field. The direction of this force coincides with the electric field, which leads to the attraction of the growing oxide particles [11]. The calculations showed that, in the investigated additive concentration range, the coagulation rate constant increases (Fig. 5, curve *2*). This agrees with the data of experimental studies. Let us estimate the ion concentration, at which the ion drag force acting on particles of the condensed phase becomes comparable to the Coulomb force. Let us assume that the motion of negatively charged particles and the singly charged positive ions occurs in an external electric field E (it may be a field generated by another particle of the condensed phase or the field of charged droplets of the metal, in a vicinity of which the formation of Al_2O_3 particles occurs). Since the Coulomb force acting on an Al_2O_3 particle ($F_c = Z_c eE$) and the ion drag force $\left(F_i = \frac{8\sqrt{2\pi}}{3} r_c^2 n_i m_i v_{T_i} u_i \left(1 + \frac{\rho_0}{2r_c}\right)\right)$ [13] (where ρ_0 – parameter characterizing the Coulomb scattering of ions on the Al_2O_3 particles, m_i and n_i – ion mass and ion concentration, v_{T_i} – thermal velocity of the ions, and $u_i = b_i E$ – drift velocity of ions in an electric field) are proportional to the electric field intensity, their ratio doesn't depend on E:

$$\frac{F_i}{F_c} = \frac{8\sqrt{\pi} r_c^2 n_i}{3 n_n \sigma_{in} Z_c}\left(1 + \frac{\rho_0}{2r_c}\right).$$

For estimates, we assume $\sigma_{in} = 5 \times 10^{-19}$ m^2, $Z_c = -20$, $T_g = 3150$ K, $m_i = 6.6 \times 10^{-26}$ kg, $r_c = 5 \times 10^{-8}$ m. Then $\frac{F_i}{F_c} \sim 4 \times 10^3 \frac{n_i}{n_n}$, and, under these conditions, the ion passion of Al_2O_3 particles is comparable with the Coulomb repulsion provided $n_i \sim (10^{-3}$–$10^{-4})n_n$. Since the concentration of neutral atoms $n_n = P/k_B T_g \sim 10^{24}$ m^{-3} ($P \sim$ ~ 0.1 MPa), the effect of ions on the interaction of submicron particles in an electric field will be noticeable, when the ion concentration reaches $n_i >$ $> 10^{20}$ m^{-3}. According to the experimental data, the growth of medium-size Al_2O_3 particles is observed at mass concentrations of K_2CO_3 more than 0.5%. This mass concentration of K_2CO_3 corresponds to the number concentration of potassium atoms in the combustion zone about 2×10^{21} m^{-3} and, at the temperature $T_g = 3150$ K, the concentration of potassium ions $n_i \sim 4 \times 10^{20}$ m^{-3}. Thus, the experimentally observed increase in the particle size of Al_2O_3 is most likely due to the increase in the coagulation rate of like-charged oxide particles at such concentrations of potassium ions, when the ion drag forces of the particles are comparable to or greater than the forces of the Coulomb interaction between Al_2O_3 particles.

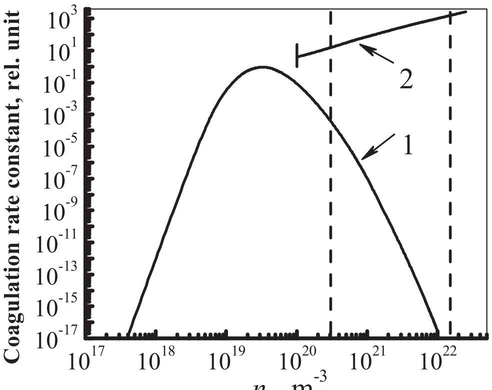

Fig. 5. The dependence between the relative coagulation rate and the concentration of potassium atoms in the plasma of products of the combustion of Al with additive K_2CO_3: *1* – the coagulation rate of charged particles; *2* – the coagulation rate with the regard for the of interaction of particles in a plasma [11]

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ДИМОВА ПЛАЗМА У ПИЛОВОМУ ПОЛУМ'Ї

Резюме

У роботі наведено результати експериментального дослідження впливу 0,1–5,0 масових відсотків добавок K_2CO_3 і KCl на дисперсність продуктів згорання газозавису частинок Al (середній діаметр частинок 4,8 мкм) у ламінарному дифузійному факелі. Експериментально виявлена екстремальна залежність середнього розміру частинок Al_2O_3 від концентрації добавки (C_a). При збільшенні концентрації добавки до 0,5% дисперсність продуктів згорання збільшується ($d_{10} \sim 50$ нм для $C_a = 0{,}5\%$). При концентрації добавки K_2CO_3 понад 0,5% спостерігалося зростання середнього розміру частинок Al_2O_3 ($d_{10} \sim 50$ нм для $C_a = 5\%$). Показано, що зміна характеру залежності середнього розміру частинок Al_2O_3 від концентрації легкоіонізуючої добавки зумовлено взаємодією пилової і іонної підсистем плазми продуктів згорання в зоні горіння факела. Проведено теоретичний розрахунок концентрації іонів у системі, при якій сила іонного захоплення порівнянна з кулонівськими силами.