Alumina nanoparticle formation under combustion of solid propellant

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Abstract

Investigation of Al_2O_3 aggregate formation under combustion of solid propellant by means of transmission electron microscopy and imaging system is carried out. Size of aggregates is about 1 μm. Size of primary composing aggregates is a few tens nm. Morphology of the alumina aggregates is studied in terms of fractal-dimension D_f which is determined to be equal to 1.6. It is established that alumina aggregates are charged both positive and negative. The typical charge per aggregate is about a few elementary charges. Some agregates are found to be dipoles. The aggregate analysed for dipole moment as an example has a charge of +20 elementary units at one end and -20 e.u. at other end. The aggregate coagulation is observed directly. It is shown that Coulomb interactions are important in coagulation.

Introduction

Dispersed aluminum is used as a fuel ingredient in solid propellants to increase the motor specific impulse and to damp acoustic combustion instability. Combustion of aluminum particles is a complex process which is not understood completely yet. During the combustion gaseous products condense to form liquid alumina nanoparticles. The mechanism of alumina nanoparticle formation is of great interest as an important stage in understanding the combustion process. Detailed knowledge of this mechanism is essential to improve motor performance and reliability. On the other hand, the question of incineration of old rockets is actual now. This incineration results in a severe ecological impact to the environment. The alumina nanoparticles formed during

incineration form aggregates of irregular shape. The morphology of these aggregates determines the transport properties in the atmosphere and also specific area which is able to adsorb dangerous incineration products like dioxines [1]. Thus, it is of great importance to investigate the aggregation mechanism and to reveal the main factors which determine the aggregate morphology.

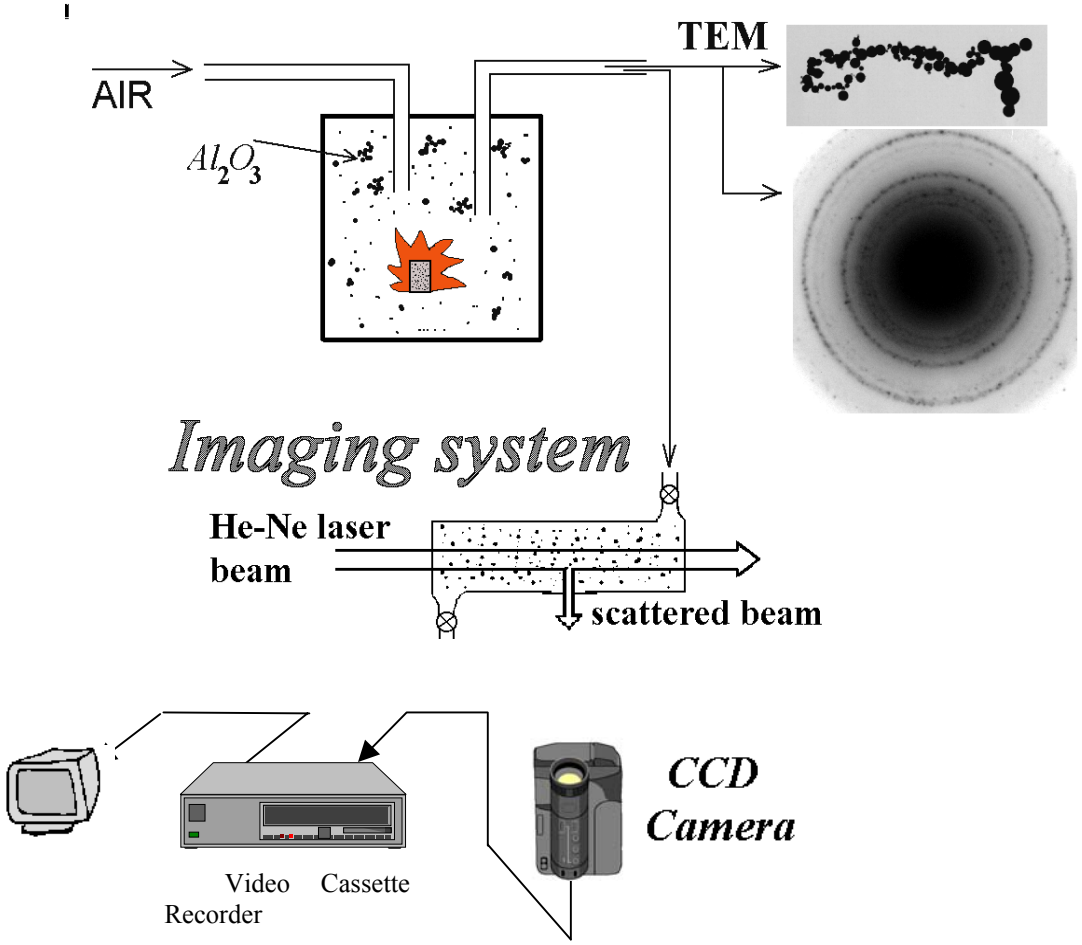
The objective of this paper is to study mechanism of alumina aggregate formation under combustion of solid rocket propellant.

Experimental

The experimental setup is schematically represented in figure 1. A small-size specimen of solid propellant (of mass about 30 mg) was ignited in the reaction chamber of 20 liters filled by air (clear of aerosol) under pressure of 1 atmosphere. The propellant consisted of polymeric binder, ammonium perchlorate and aluminum particles of size 5 - 15 μm. The combustion time for specimen was about 5 s. During the combustion process initial aluminum particles are sintered and the burning agglomerate droplets were ejected to the ambient air producing Al_2O_3 aerosol nanoparticles with size about 30 mn. For the analysis by TEM - transmission electron microscopy (size, morphology and crystal structure of nanoparticles), and for observation in imaging system the air with nanoparticles was sucked for sampling [2]. The time *t* between the beginning of combustion and sampling was varied in the range 1 - 20 min. Sampling for TEM was carried out thermophoretically. The imaging system was composed by an optically accessible cell to which a portion of Al_2O_3 was injected. A He-Ne laser beam passed through this volume. The scattered light was collected at the angle of 90° through a flat window by a CCD camera producing an image of aggregates of nanoparticles. It was possible to observe the aggregate shape when the size was greater than 2 μm. When the size was lesser the aggregates were seen as luminous spots. This imaging system allows to see in real time (25 frames per second) the coagulation process. It was possible also to apply an homogeneous electric field in the optical cell. In this case the drift of the aggregates along the field was observed giving the

information on the aggregate electric charge. The change of the electric field polarity resulted in rotations of some aggregates. The rotation velocity gave an information on the dipole moment of these aggregates.

Figire 1: Schematic diagram of the experimental setup.



Results

Al_2O_3 nanoparticles generated by the combustion of Al droplet form aggregates composed by small spherical primary particles. Examples of these aggregates are given in figure 2. The aggregate radius *R* was determined from TEM images as:

$$R = 0.5\sqrt{WL} \ , \qquad (1)$$

where *W* and *L* are the width and length of the circumscribed rectangle. Figure 3 shows the mean arithmetic radius of aggregates as a function of coagulation

time in the reaction volume (i. e. time from the beginning of combustion to the sampling moment).

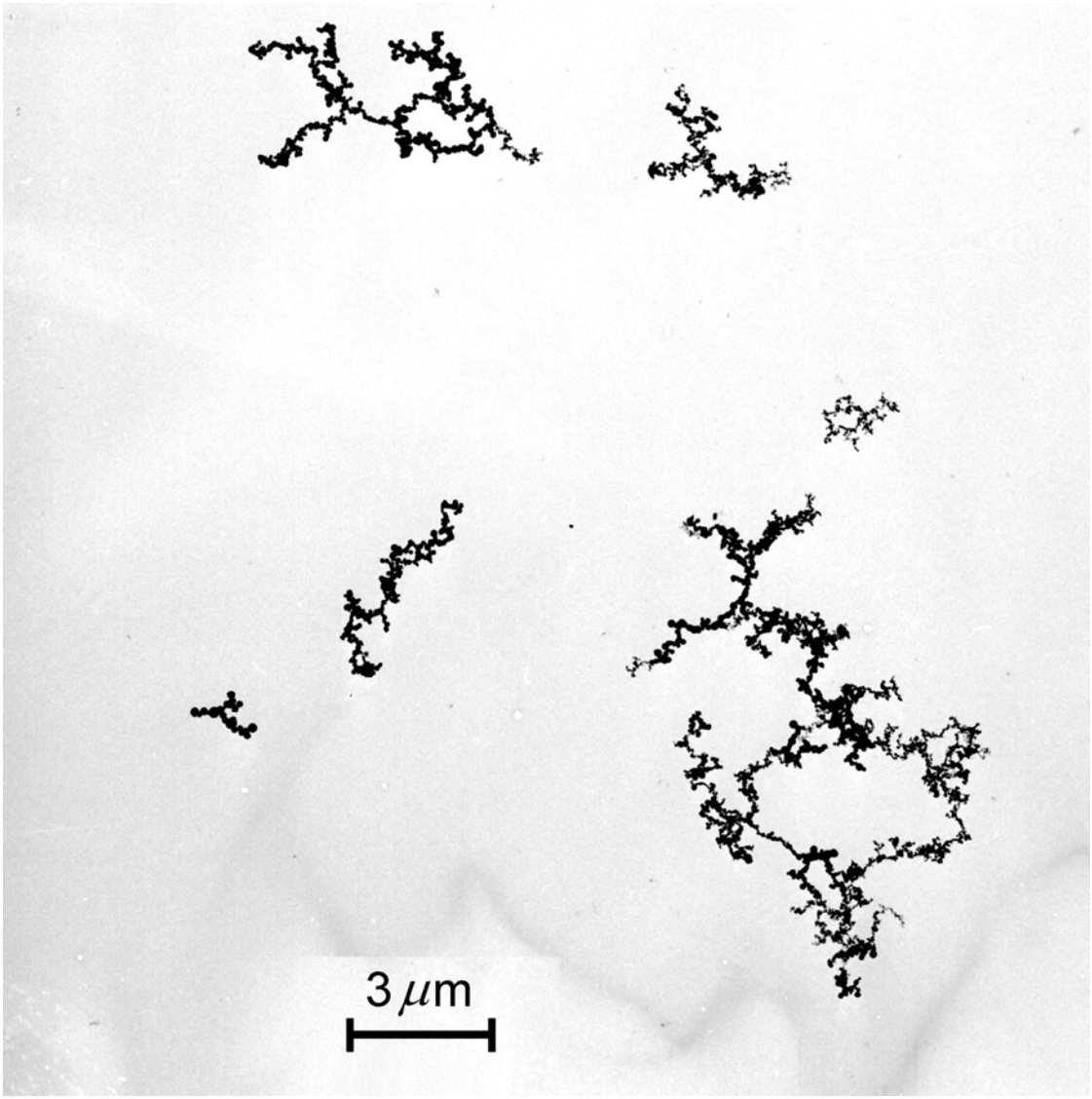


Figure 2: TEM images of Al_2O_3 aggregates sampled from the reaction volume 6 min after combustion of solid rocket propellant.

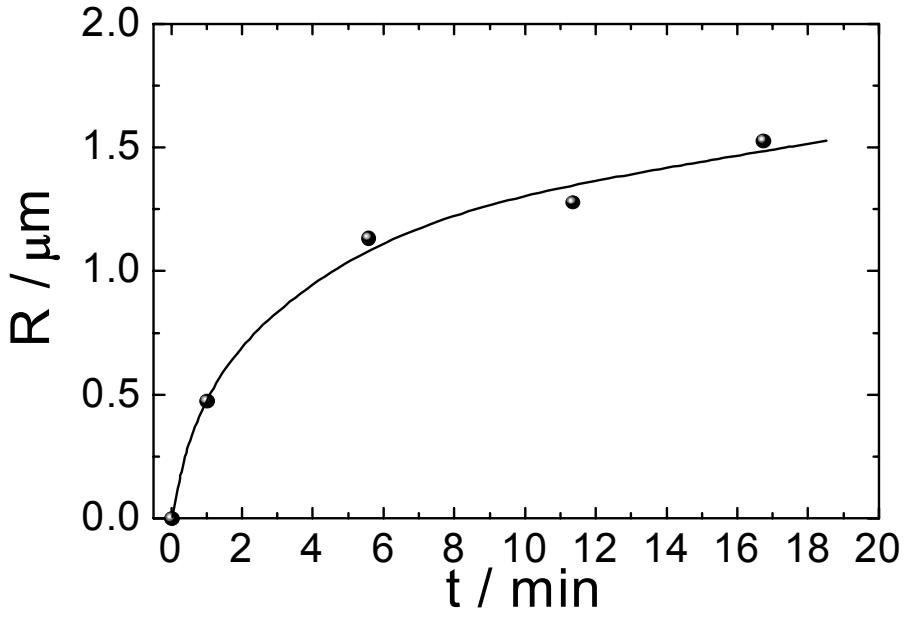


Figure 3: Mean arithmetic radius of aggregates *vs* coagulation time.

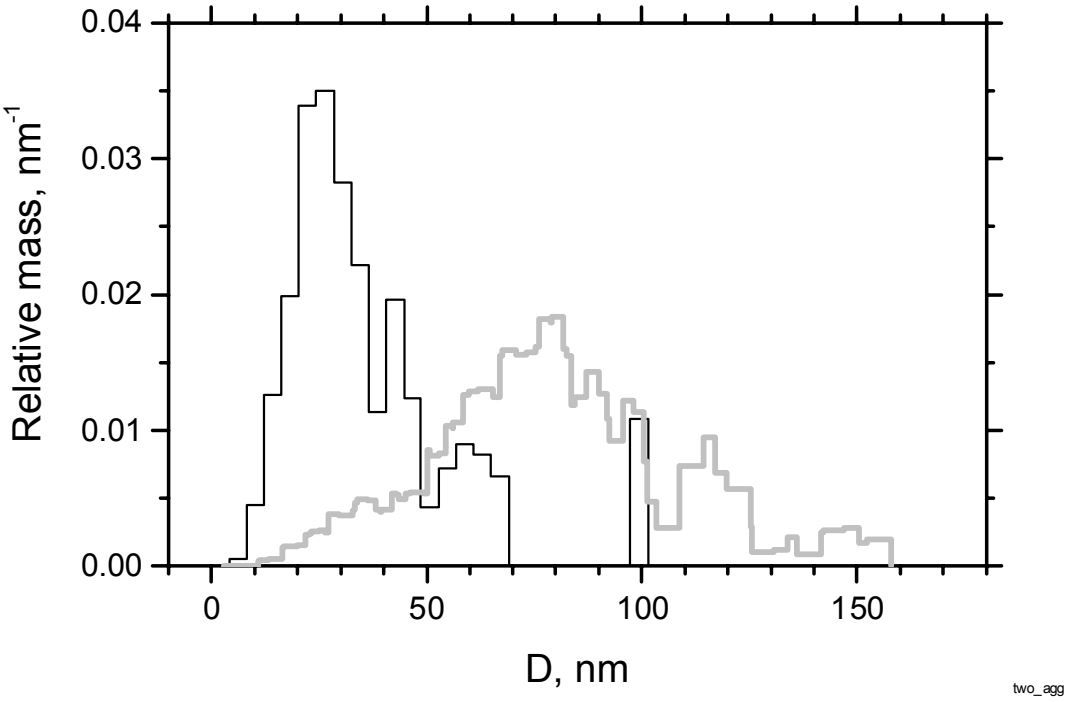


Figure 4: Mass size distribution of primary particles for two aggregates.

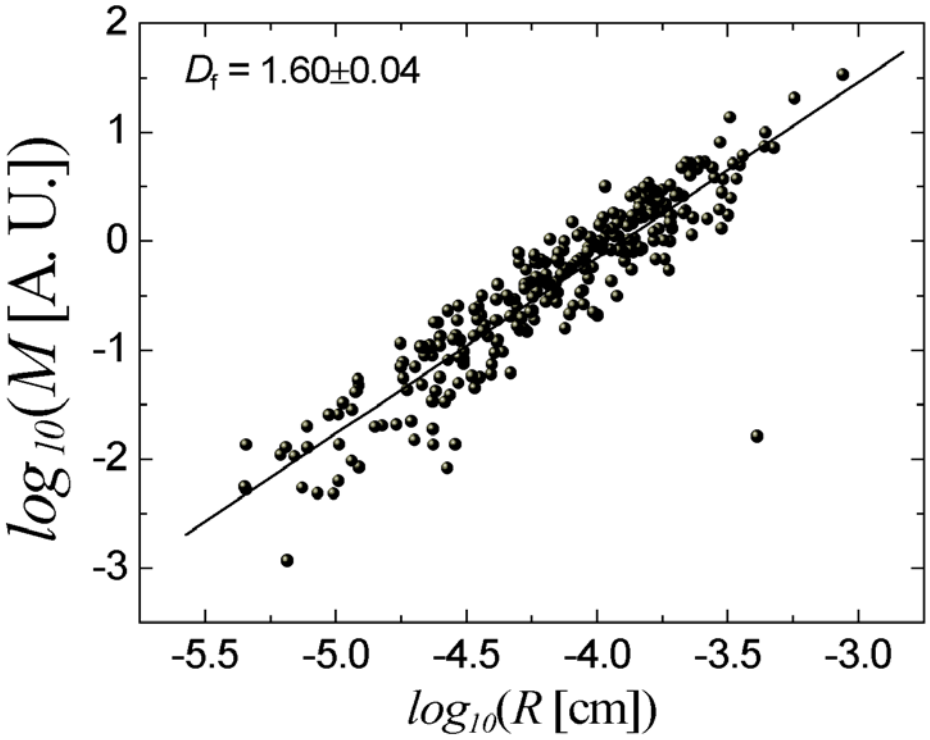
It was found that the average size of primary particles varies from aggregate to aggregate. Figure 4 demonstrates mass size distribution of primary particles in

two different aggregates. One can see a considerable difference between these two size spectra. This difference may indicates that the primary particles for these two aggregates were formed under different conditions. TEM analysis in the regime of electron diffraction showed that nanoparticles consist of γ-Al_2O_3 (see the diffraction pattern in Figure 1).

The morphology of the aggregates was described in terms of fractal-like dimension D_f which was determined from a power law expression connecting the aggregate mass M and radius:

$$M \propto R^{D_f} \quad . \tag{2}$$

The mass of each aggregate considered in a TEM micrograph was plotted in coordinates log$M$ - log$R$. Fractal-like dimension determined from this graph by linear fit was D_f = 1.60 $\pm$ 0.04, figure 5).



Fiugure 5: Determination of fractal-like dimension for Al_2O_3 aggregates.

M *vs* ***R*** plots of TEM data for Al_2O_3 aggregates. M is the agglomerate mass; $R = \frac{1}{2}\sqrt{LW}$, where W and L are the width and length of the circumscribed rectangle. Solid line corresponds to the equation: $\boldsymbol{M} \propto \boldsymbol{R}^{\boldsymbol{D_f}}$ with D_f = 1.6.

Such value of fractal-like dimension is too low to explain it by an ordinary diffusion limited cluster-cluster aggregation [3]. One of the explanation for this low value of D_f could be the long range interactions between colliding aggregates. To check out if the aggregates has electric charge we observed movement of the aggregates in the presence of homogeneous electric field using an imaging system. It was found that all the aggregates were moving along the electric fields which proves the fact that the aggregates are charged.

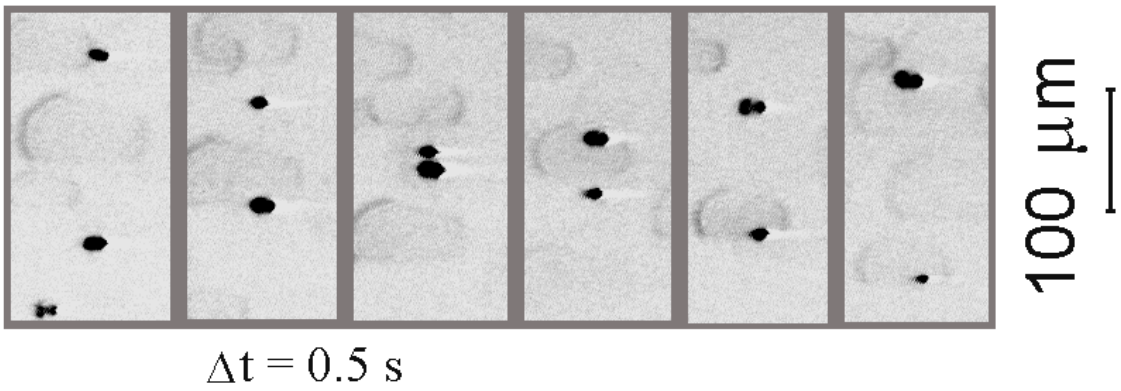


Figure 6: Movement of (+) and (–) charged aggregate in the electric field.
Series of frames illustrating the movement of aggregate in the homogeneous electric field of 160 V/cm. The frames are separated by a time interval Δt = 0.5 s. Time increases from left to right.

Figure 6 demonstrates the movement of aggregates in the electric field. A six frames separated by a time interval of 0.5 s are represented. One can see that one aggregate is moving upwards (negative charged) and the other one is moving downwards (positive charged). The charge of aggregates was estimated from the balance between the drag force and the electric force:

$$eE = 6\pi R_{eff} V \eta. \qquad (3)$$

where e is the electric charge of the aggregate, E is the electric field strength, R_{eff} is the effective radius of the aggregate [3, 4], V is the velocity of aggregate movement, η is the viscosity of the air. The charge distribution of the aggregates determined by the imaging system observation is presented in the figure 7. One can see that there are both positive and negative aggregates

formed in combustion of solid rocket propellant. The typical charge of aggregates is a few elementary charges.

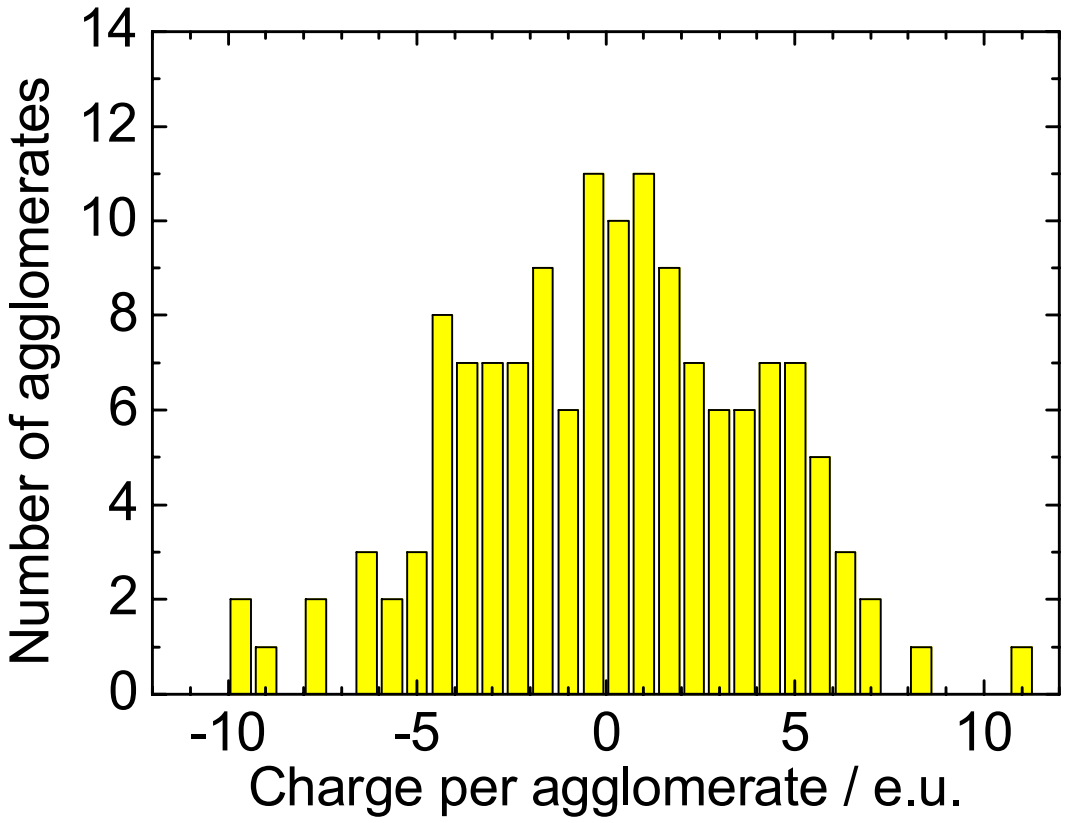


Figure 7: Frequency distribution of aggregates by value of electric charge.

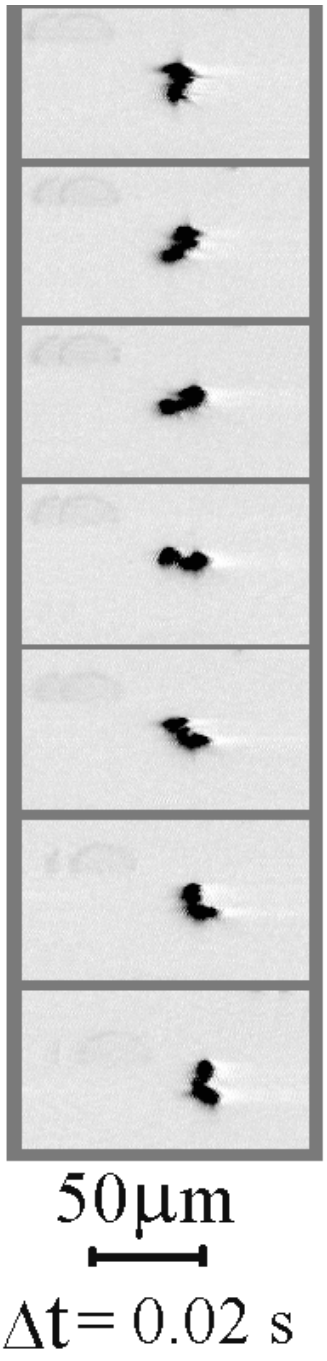


Figure 8:

Series of images illustrating the aggregate rotation after the switching the electric field polarity. The frames are separated by a time interval Δt = 0.02 s. (shown in the Figure). Time increases from top to bottom.

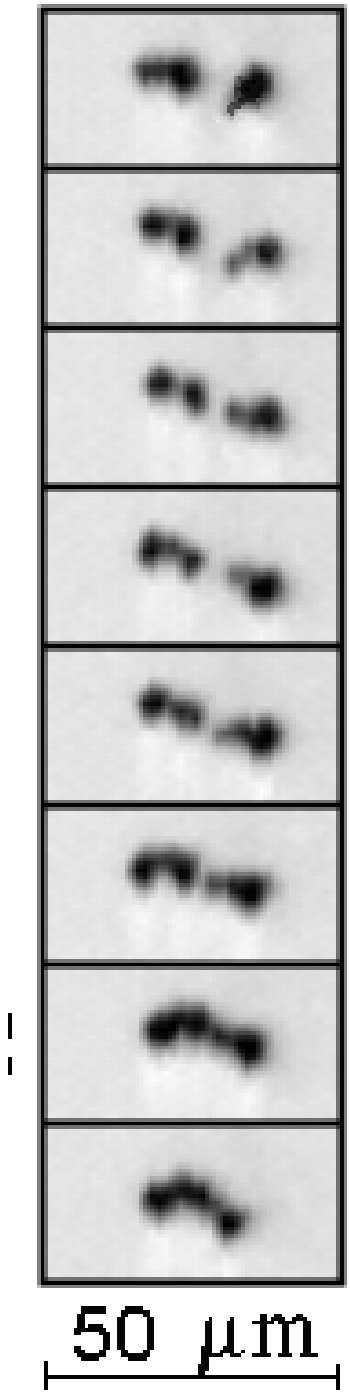


Figure 9:

Series of frames illustrating sticking of two charged aggregates. Time increasing from top to bottom. Time interval between frames is 0.04 s.

Some aggregates are dipoles. This fact is demonstrated by rotations of aggregates when changing the electric field polarity, figure 8.

Figure 9 demonstrates results of direct observation of aggregate - aggregate collision accompanied by Coulomb interaction. In figure 10 the distance between the aggregates *vs* time is presented. One can see that the velocity of mutual approach increases with time and reaches maximum value by the moment of collision.

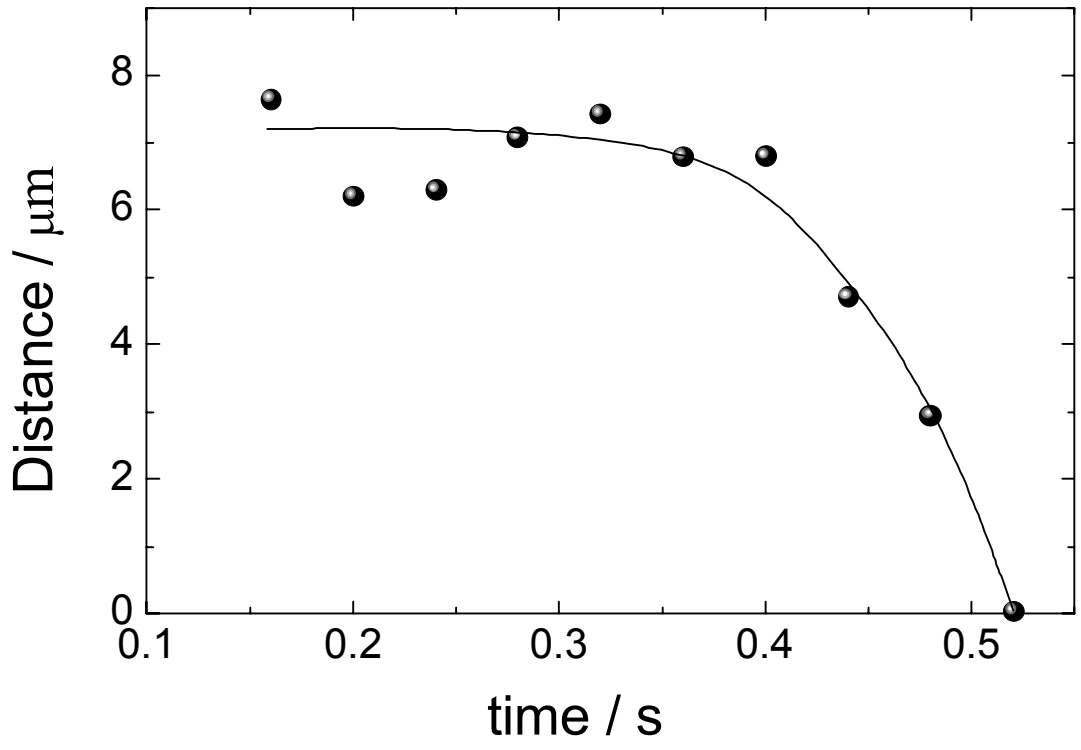


Figure 10: Distance between the aggregates represented in Fig. 9 vs. time

Discussion

Formation of liquid Al_2O_3 nanoparticles due to condensation reactions in the smoke envelope surrounding the burning aluminum particle is accompanied by the coagulation + coalescence process resulting to formation of large nanoparticles of size about a few tens nanometers. In the outlying part of the smoke envelope the temperature is reduced as regards to the nearest to the Al droplets zones. Thus a crystallisation occurs in the regions with decreased temperature [5]. As a result, the further evolution of the Al_2O_3 nanoparticles proceeds through the aggregation process resulting to formation of irregular aggregates, figure 2 composed by small primary particles. Average size of primary particles varies for different aggregates (figure 4). Presumable, it means that the aggregates were formed in zones with different concentration of Al_2O_3.

Figures 6 and 7 show that forming aggregates of Al_2O_3 are charged. Most probable reason for this electric charge is thermoionic emission from particles at high temperature (3800 - 2000 K) in the smoke envelope.

Figure 8 shows the rotation of an aggregate when the field polarity was switched that testify the aggregate is a dipole. From the rotation velocity one can estimate the moment of force acting to the aggregate in the moment when the field polarity was changed. The aggregate rotation is governed by the equation:

$$d\theta/dt = B_\omega M_\theta \ , \qquad (4)$$

where θ is the rotation angle, B_ω is the "rotation mobility", M_θ is the moment of the external force. To estimate the rotation mobility we approximate the aggregate by an ellipsoid of revolution with the ratio of the major axis length to the minor axis length equal to 6. In this case we have [6]:

$$B_\omega = 5.9(\pi\eta L^3)^{-1} . \qquad (5)$$

Thus, from the values of $d\theta/dt$ we can estimate the moment of force using equations (4) and (5). This value of M_θ give an information about the dipole moment of the aggregate. Our estimations showed that the revolution of the aggregate corresponds to the situation when there is a charge about +20 elementary units at one end and –20 at the other end.

Conclusions

The experimental data obtained demonstrate that combustion aluminum droplets forming at aluminized solid propellant burning results in formation of aggregates of size about 1 μm composed of small nanoparticles of Al_2O_3 of size of a few tens of nanometers. The fractal-like dimension of these aggregates is D_f = 1.6 which is too small to explain by the ordinary mechanism of diffusion-limited cluster-cluster aggregation. The reason for this low D_f is evidently an electric charge of the aggregates. We determined that electric charge is a few elementary charges. Both positive and negative aggregates were observed. Some of the aggregates are dipoles. Thus the conclusion is that Coulomb interactions can be essential in Al_2O_3 aggregate formation and evolution.

Acknowledgments

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