

Thixotropic metal aerosols of the near-ground atmospheric layer

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Chemical and technological aspects of the interaction of man-caused electroblasting aluminum aerosols with the air and water are considered. It is shown that aerosols in the solid disperse phase are especially dangerous, since they easily ignite in air and release a great amount of heat while burning. In water they evolve explosive "hot" hydrogen. The small size of particles of such aerosols causes significant self-heating at their interaction with reagents. This leads to stabilization of final products unusual for the bulky state.

Introduction

One of the problems in the research field of atmospheric optics is the study of the composition and properties of possible components of atmospheric aerosol that may be envisioned in accordance with the tendencies of the industrial development. Development of ferrous and nonferrous metallurgy in Russia, on the one hand, and expected appearance of the nanotechnologies,¹ on the other hand, will contribute to the increasing content of chemically active solid-phase components of aerosol in the near-ground atmospheric layer. Such man-caused aerosols with a solid disperse phase (hereinafter, solid aerosols) are not only ecologically dangerous, but often fire-hazardous and explosive as well.² This class includes a wide variety of substances: metals, alloys, sulfur, phosphorus, sugar, flour, polymers, etc.

Great amount of solid aerosols are emitted into the atmosphere, for example, as a product of the volcanic activity (volcanic dust) or burning of ash-containing solid fuels (smokes of boiler houses). Solid aerosols can be also by-products of cement and silicate works. However, such smokes are usually fire-safe, since they mostly consist of metal and non-metal oxides. But if a technological cycle includes, for example, flour (grain elevators, etc.), coal dust (boiler houses, coal mining, etc.), and metals (plants producing metal powders, smelting plants, etc.), the situation is different. In the open air and in water, such aerosols burn with release of a huge amount of heat at interaction with water and oxygen and nitrogen from air. The generation and accumulation of such aerosols in a closed volume is extremely dangerous. As a rule, these aerosols are sensitive to a local thermal pulse, spark, etc. Burning often becomes an explosion with strong destruction consequences and even victims.

The study of the structure and properties of solid aerosols as specific atmospheric pollutants is of great interest for prediction and prevention of the emergencies.

Objects for the study

We have studied the behavior of solid metal aerosols in the atmosphere and water bodies (reactions of metal aerosols with air and water). Such aerosols are characterized by thixotropy (inversion of disperse medium and disperse phase). Metal (Al, Fe, Cu, Ni, Co, Ti, etc.) aerosols were produced by electrical explosion of conductors in the atmosphere of inert gases (Ar, He, N₂). When active gaseous media are used, electrical explosion of conductors can produce aerosols of chemical compounds.³

Electrical explosion of conductors is a nonequilibrium process, therefore thus produced aerosols have potentially high activity as compared to that of analogous aerosols produced, for example, by the evaporation/condensation or sol-gel methods.⁴ At cooling and sedimentation, the electroblasting aerosols condense to aerogels⁵ (hundreds g/m³ of air), which are converted back to concentrated aerosols at a weak mechanical effect. Aluminum aerosols have no metal lustre (they are black); their specific area is 10–30 m²/g at the surface-mean diameter of a particle from 10 to 100 nm; the particle size distribution is bimodal; an oxide shell on particles after soft passivating in air is from 2 to 5 nm thick. According to the data of X-ray phase analysis, a spherical particle is metal aluminum covered with X-ray amorphous oxide.^{6,7} The use of the term "powders" for such system is poorly justified, since they are thixotropic aerosols in the Ostwald classification of colloid systems.⁸

A model of an ultrafine particle of the disperse phase of a metal aerosol was proposed in Ref. 9. The particle has a non-typical colloid structure with a double electrical layer formed at slow passivating by atmospheric constituents and in the processes of charge and mass transfer. This layer provides for stability of particles and powders at heating and interaction with reagents. As will be shown below, the colloid structure of aerogels is destructed at their interaction with atmospheric constituents and water. Large bulk of information is

now accumulated on the behavior of metal particles in the atmosphere.^{10,11} However, most of the papers ignore the structure of individual particles.¹²

Interaction of metal aerogels with air

Interaction of metal aerogels with air proceeds as burning. We consider it here using electroblasting aluminum aerogels as an example. This approach applies, because some regularities are characteristic for other metal aerogels as well.²

There are papers devoted to the study of ignition and burning of individual aluminum particles.^{13,14} As a rule, particles were sampled from ASD-1 and ASD-4 powders produced by the USSR industry. The studied spherical particles had a minimum diameter of 5–10 μm . The ignition temperature for such particles, as is seen from Table 1, far exceeds the melting temperature of aluminum (660°C).

Table 1. Dependence of the ignition temperature on the particle diameter

Particle diameter, μm	Ignition temperature, °C	Reference
6	995	
20	1580	
30	1800	15
40	2100	
130	2050	
165	2300–2700	13
400	2090 (pyrometer)	
680	2070 \pm 50 (thermocouple)	14

Unfortunately, the methods of research into the ignition and burning of individual particles from Refs. 13–15 are inapplicable to ultrafine particles (surface-mean diameter of 10–100 nm). Besides, it is practically impossible to separate out single ultrafine particle from aerogel. Therefore, interaction with air was studied for a set of particles in aerogel. This study does not require specialized equipment (explosion chamber) in contrast to the study of aerosols.

Burning of the aluminum aerosols consists of several stages.¹⁶ The energy threshold (beginning of oxidation of an ultrafine particle at slight local heating) is overcome, likely, primarily due to reducing the oxygen atoms chemisorbed on a particle surface. At the initial stage of oxidation, oxygen from air does not play a significant part, since burnout of the surface fragment Al-O• having an unpaired electron (•) is far more energy-efficient. This is confirmed by the fact that the gas pressure at the first stage of burning in a closed bomb changes insignificantly: air almost does not burn out. However, at the second stage, the pressure decreases significantly because of nitrogen burning out from the air (Fig. 1).

The low ignition temperature (540°C, Ref. 6) is explained by relaxation of the energy-saturated structure of the ultrafine particle. As a result, the particle warms up significantly at the first stage of

oxidation, the reaction is initiated, and the reaction heat is localized inside the particle and then inside the aerogel volume. The temperature can far exceed the aluminum melting temperature already at the first stage. This likely leads to partial evaporation of aluminum and significantly shifts the equilibrium of the reaction (1) to the right:

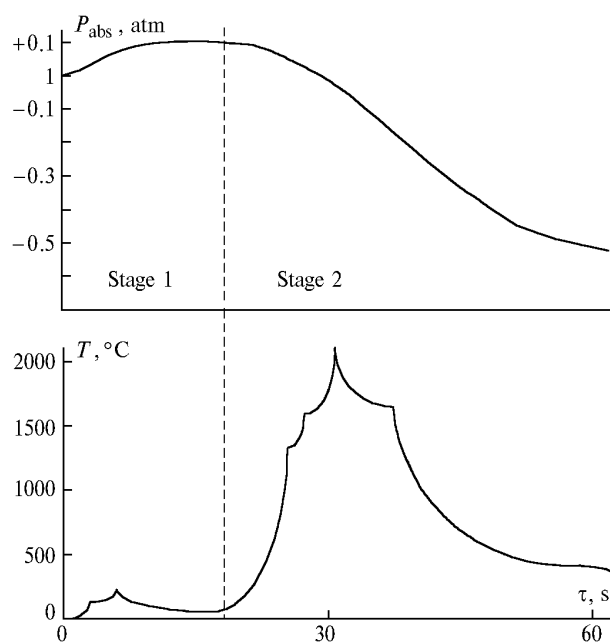
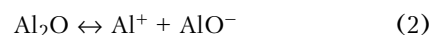


Fig. 1. Oscillogram of burning of the electroblasting aluminum aerogel (FR-11 photorecorder, MP-3 vacuum manometer, N-117/1 loop oscillograph).

In converting to the gas phase, the reaction becomes sharply self-accelerated due to the collective effect. This leads to almost adiabatic burning conditions. It is just this process that is observed at the second stage of burning. In the aerogel volume, the temperature at burning can exceed the aluminum boiling point and the melting temperature of aluminum oxide (2520 and 2044°C, respectively). As a result of intense reactions of oxidation and high temperatures, electrophilic cation formed due to dissociation (reaction 2)



likely interacts in the gas phase with the nitrogen molecule¹⁷ and forms aluminum nitride or oxynitride, if the reaction is not completed. Nitride formed in the gas phase consumes a significant part of the heat from the reaction zone. This lowers the temperature and stabilizes the phase of nitride.

At burning of very active aluminum aerogels in air, the processes of self-organization are observed. At oxidation in air under conditions of a Q-1500D derivatograph, up to four peaks/dips in the oxidation rate are observed on TG (DTG) and DTA curves (Fig. 2).

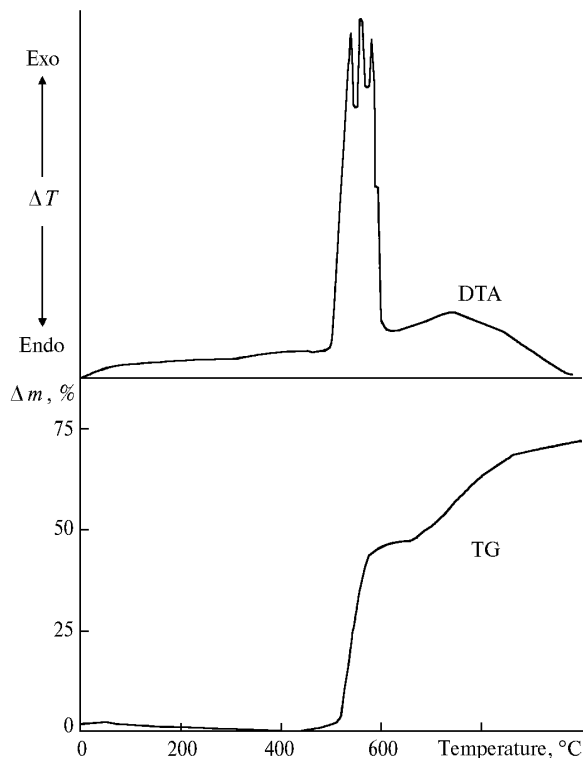


Fig. 2. Derivatogram of the electroblasting aluminum aerogel ($m = 50.2$ mg) in air; $v = 10^\circ/\text{min}$.

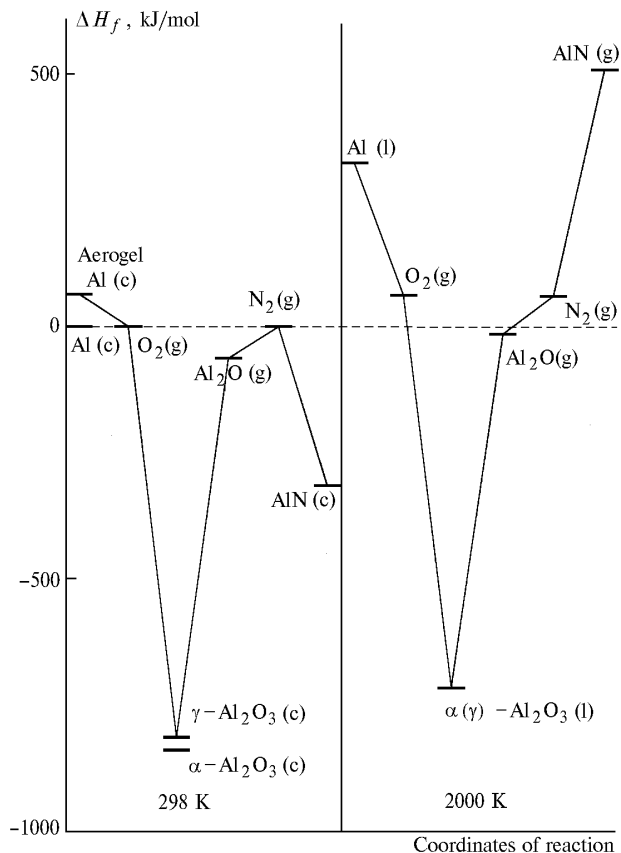


Fig. 3. Thermodynamic scheme of formation of the phase of aluminum nitride at burning of electroblasting aluminum aerogel [subscripts denote the condensed (c), liquid (l), and gaseous (g) states].

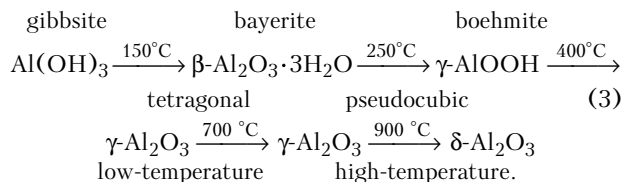
The sharp increase of the oxidation rate leads to the increase of temperature and to the start of the endothermic processes. This, in turn, favors a decrease in temperature, in the oxidation rate, and termination of the endothermic processes. Nitride is condensed, being slightly oxidized on the surface. This leads to the decay of the burning reaction. The theory of burning of aluminum aerogels in air is confirmed by the thermodynamic scheme of formation of the aluminum nitride at high temperatures (Fig. 3).

In accordance with the scheme, the sole exothermic reaction at $T = 2000$ K is the aluminum oxidation by oxygen, whereas formation of nitride requires even more heat than it is released.

Thus, at burning of metal aerogels (in the example with Al) in open air, high temperature in combination with high chemical activity of fine particles leads to prevalent burnout of nitrogen from air. At burning of metal aerosols (wider spraying), the degree of their conversion into products is even higher ($> 85\%$), and this leads to burnout of large amounts of air and fires even under deficient oxygen content.

Interaction of liophilic aluminum hydrosols with water

Because of small size and structure peculiarities, ultrafine aluminum particles exhibit the properties of ordinary metal sodium in the bulk state in reactions with water and organic reagents.¹⁸ As ultrafine particles fall in water, they initially are distributed over the volume thus forming a colloid system, or the liophilic hydrosol, i.e., they are readily moistened by water in some time. After a short induction period (several minutes), the violent reaction starts of aluminum with water with the release of hydrogen. Because of difficulties in experimentally determining the temperature of reaction with the participation of individual particles, final products are used as indicators of temperature in the chemical reaction. The criterion of choosing such reactions can be the temperature dependence of the phase and chemical composition of the products. The reaction of aluminum with water proved to be very convenient for such studies. Conditions of oxidation in water are softer than in the air, and this allows the regularities connected with the peculiarities of ultrafine particles participation in the processes to be revealed. In heating of aluminum hydroxide, the following series of transformations is observed¹⁹:

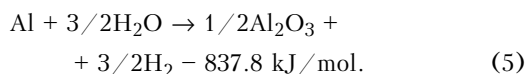
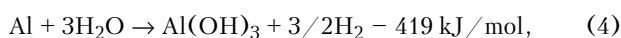


In contrast to coarse particles, aluminum hydrosols are characterized by high degree of conversion into products (up to 100%). At the temperature of water lower than 40°C the main product of interaction is crystal aluminum hydroxide, and at the temperatures above $40\text{--}60^\circ\text{C}$ the main products of the reaction are amorphous aluminum oxide and $\gamma\text{-AlOOH}$ (pseudocubic boehmite) (Table 2).

Table 2. Phase composition of the products of aluminum hydrosol interaction with water

Specific surface area of disperse Al in aerogel, m ² /g	Temperature of water, °C	Phase composition of products, % mass			
		Al(OH) ₃	AlOOH	Al ₂ O ₃ (amorphous)	Al ⁰
8.1±1.2	15	18	36	39	5
	55	0	10	84	6
13.5±0.8	15	0	26	72	2
	55	0	6	88	6

The increase of water temperature and the use of admixtures of organic reagents allow one not only to increase the reaction rate, but also to direct the process toward the realization of the mechanism with high heat release ΔH_r . This, in its turn, increases the rate of reactions²⁰:



Electroblasting titanium and ferrous hydrosols react with water in a similar way at a significant self-heating. A peculiarity is the formation of lower oxides at oxidation of not passivated metals by water (Ti₂O₃ and FeO, respectively).²¹

The study of the strength of thermal effects at interaction of aluminum hydrosol with water using an MKDP-20 microcalorimeter showed that the increase in water temperature by only 10°C (from 60 to 70°C) led to the increase of the heat release from (16.7±4.0) to (18.1±1.0) kJ/mol (Ref. 20).

Thus, aluminum hydrosols react with water at low temperature almost completely up to the final product with the formation of significant amounts of "hot" hydrogen as one of the high-temperature products. This fact makes them even more hazardous, since "hot" hydrogen easily forms very sensitive explosive mixtures with air in a wide range of concentrations.

Conclusions

The results obtained on the interaction of aluminum aerogels with air and water showed the following.

At the first stage of burning of aluminum aerogels in a closed bomb, the pressure changes insignificantly. At the second stage, nitrogen and oxygen burn out from air. This creates rarity in the bomb.

The burning rate of aluminum aerogels in air is so high that heat released in burning has no time to dissipate, and only the endothermic processes limit the growth of the temperature.

The interaction of aluminum aerogels with water leads to a significant self-heating: reacting aluminum particles in water have the temperature that exceeds by hundreds degrees the temperature of the water body. The product of interaction is "hot" hydrogen that can be accumulated at a high reaction rate and form explosive mixtures with air.

The increase/decrease of the temperature at burning of aluminum aerogels can repeat several (up to four) times. This is an element of self-organization.

Thus, the emissions of metal aerogels into the near-ground atmospheric layer are ecologically hazardous, and, what's more important, they introduce elements of high fire and explosion risk.

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