

Physico-chemical properties of condensed metal aerosols and their burning in air

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The structure and properties of condensates of aerosols of metal aerogels (density 0.1–0.2 g/cm³) produced under strongly non-equilibrium conditions as a result of electric explosion of conductors are analyzed. It is shown that the properties of small metal particles depend on the area of the specific surface and the ratio between the heat for formation of a substance in the form of small particles and the heat of melting. As the particle size decreases, the melting temperature of metals decreases, and spontaneous sintering occurs accompanied by the decrease of the specific surface of aerogels in the disperse phase. The properties of electric-explosion metal aerogels differ widely from those of aerogels produced under equilibrium conditions. A particular attention is paid to peculiarities of burning of metal aerogels in the air atmosphere associated with the chemical fixation of nitrogen from air and stabilization of aluminum nitride in the resulting burning products for aluminum–air aerogels.

Study of physico-chemical properties of small particles and powders is urgent because of the following reasons. Determination of actual conditions for existence of both individual particles and their sets in the form of powders is interesting from the theoretical and practical viewpoints. Dispersing of solid bodies changes their thermodynamic, electrochemical, spectral, structural, thermophysical, and other properties.¹ If small particles are produced by associative synthesis, the characteristics of a substance also change. Just the values of these characteristics carry the information about stable, metastable, or unstable state of small particles and powders. The change in the characteristics results in the change in the reactivity of powders, in particular, stability to oxidation.

At the same time, it is still the problem to justify the special state of a matter as small particles and to elaborate the terminology for identifying this state. Classification of thin films, porous bodies, whiskers, etc. as small-size objects is now under discussion because the above-listed objects have not such properties as self-closeness and small isolated volume.

An important factor in formation of the structure and properties of small particles is the conditions of their production, first of all, the power and value of energy impact. An object of our study is a spherical metal particle formed under equilibrium conditions. As the particle diameter decreases, the curvature of its surface increases, as well as the part of atoms being on the surface. Thus, the mechanic stress of chemical bonds between atoms on the surface increases, and the amplitude of oscillation of atoms on the surface increases too.² The influence of the surface on characteristics of a particle is observed if particle diameter is less than 10 nm. The objective criterion for estimating the influence of the particle size (size factor) on particle stability may be the enthalpy of formation

of one mole of a substance in the form of small particles (ΔH_f) equal to the standard heat of melting of the substance (ΔH_m). The choice $\Delta H_f \approx \Delta H_m$ is of principal importance: if $\Delta H_f \geq \Delta H_m$, then the thermodynamic state of a particle must formally correspond to the liquid phase.

Despite the experimentally observed state of particles with $\Delta H_f \geq \Delta H_m$ remains solid, in some characteristics such particles are close to the liquid state. Conservation of the solid state of small particles in their principal characteristics at $\Delta H_f \geq \Delta H_m$ is connected with the mutual influence of the surface and volume. This influence results in stabilization of the equilibrium crystal or amorphous structure of a substance in these particles.² An individual particle of any size in the inert atmosphere can exist an infinitely long time. However, contact of small particles with diameters less than 30 nm leads to their sintering at the room temperature accompanied by the decrease in the area of specific surface (S_{sp}). To increase the stability of such particles, they can be precipitated on a substrate or coated with a film-forming substance or reactive substances in small amounts. In the latter case the particle becomes a macromolecule.³ To store powders, specialized liquids can also be used. The calculated values of the melting temperature (T) of potassium and silver spherical particles are given in the table (Ref. 4).

r , nm	Potassium ($T_x^* = 336$ K)		Silver ($T_x = 1235$ K)	
	T , K	ΔT , K	T , K	ΔT , K
20	50	286	593	640
30	144	192	800	433
50	222	114	973	260
100	279	57	1110	123

* Melting temperature of a metal in the massive state.

Thus, individual small particles produced in inert media under equilibrium conditions are stable during storage but unstable to sintering in the case of contact of many particles. The probability of sintering of less disperse powders at the room temperature decreases; if the diameter of particles is larger than $\sim 1 \mu\text{m}$, then the probability of sintering sharply decreases too.

Another aspect of stability of small particles is their interaction with atmospheric components, i.e., oxidation accompanied by heating. Most metals in the form of powders with particle size less $0.1 \mu\text{m}$ are pyrophoric, that is, susceptible to spontaneous ignition under room temperature. The exclusion among widely used metals is zirconium powder, which self-ignites if the mean particle diameter is less than $3 \mu\text{m}$ (Ref. 5). Particles of irregular shape and any other shape different from the spherical one have, as a rule, lower stability to oxidation. At slow oxidation under controlled conditions, stabilization of small particles in air is possible.

It is shown experimentally that as the particle diameter decreases in the range $0.1 - 0.01 \mu\text{m}$, the oxide coating becomes thinner.² As was found, for small particles, in contrast to micron-size particles, oxidation is retarded by formation of the electrostatic potential, rather than diffusion limit, because the former prevents transfer of an oxidizing-reducing agent. Depending on the nature of the substance of a small particle, the thickness of the oxide-hydroxide shell is from one to several nanometers. It should be noted that spherical metal particles having diameter less than $30 - 10 \text{ nm}$ and formed under equilibrium conditions cannot, as a rule, be stabilized in air: particles of such size contain likely not enough substance to form the protecting shell.

If particles are formed under strongly nonequilibrium and extremal conditions, for example, under conditions of electric explosion of conductors (EEC) (Ref. 6), metal aerosols resulting from spraying by high-power current pulses ($j \geq 10^{10} \text{ A/m}^2$) form aerogels in the process of precipitation. The presence of chemically active gas medium leads to formation of aerogels of chemical compounds (oxides, nitrides, etc.). If metal aerogels are produced in the medium of chemically inert gases (helium, argon), then small particles are coated by gas shell preventing contact between particles and sintering. The stability of such aerogels is caused both by the gas shell and by the gases held by the capillary-fractal structure.

In the process of desorption of gases from the gas shell, the temperature in the aerogel volume decreases according to thermocouple measurements. At slow passivation the following processes take place: gas-medium desorption, adsorption of air components, and formation of the oxide-hydroxide protecting shell. The last process is strongly exothermal, and self-ignition of aerogels is possible at intensification of the oxidation process. After slow passivation the aerogels are stable in air and can be stored for a long time in the dry atmosphere.

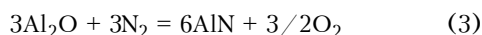
In the process of passivation, the specific surface area (S_{sp}) of the solid phase of aerogels increases (by 30% for aluminum); then during storage S_{sp} decreases by 30 - 40% several days later. Initially, the surface becomes looser due to formation of oxidation products, then S_{sp} decreases as a result of crystallization and condensation of the products. According to photoelectron spectra, the initially formed products contain oxygen-poor compounds, and at long storage the oxygen content becomes superstoichiometric. The most scientifically justified model of the metal aerogel particle is the model, in which the stability to oxidation is determined by the value of the electric potential preventing diffusion of the oxidizing agent inward the particle. The electric-explosion aerogels passivated by slow oxidation markedly differ in the structure and properties from the aerogels produced under equilibrium conditions.

It is found experimentally that under certain EEC conditions it is possible to obtain thinner oxide-hydroxide films on the surface of particles. In this case the electric-explosion metal powders, which are stable in air, contain 5-15% more non-oxidized metal. Such powders have low bulk density, for example, for the aluminum powder $\sim 0.1 \text{ kg/dm}^3$, what makes up 5-10% of the density of compact metal. In contrast to industrial powders, aerogels have low thermal conductivity, and relatively low energy is needed to initiate their burning.

The study of the process of metal aerogel burning in the atmosphere of air and less strong oxidizing agents is of great practical interest in view of emergency situations in production, mechanical and chemical processing of metal materials (cutting, welding, fatigue wear, melting, plasma and high-temperature chemical processing). Under certain condition large amounts of metal aerogel may be produced by these processes.

It is also interesting to study the peculiarities of burning of the metal aerogel produced in electric explosion of conductors as a result of cooling of aerosols, which are the products of explosion of metal wires traversing a high-power current pulse. High-temperature products of explosion fly apart in the closed chamber with the speed up to several kilometers per second. Cooling fast, the aerosols - explosion products - are condensed with formation of metal aerogels (the surface mean diameter of particles of the disperse medium is from 10 to 100 nm). The aerogels obtained in such a way are capable to spontaneous ignition and burning in open air with formation of nitrogen-containing products. After initiation of ignition by local heating with a Nichrome heating element ($T_{\text{ign}} = 510 - 540^\circ\text{C}$),⁶ overlapping thermal waves propagate over the surface of a sample. The temperature of burning of aerogels of aluminum superfine powders (SFP's) was measured with tungsten-rhenium thermocouples with a junction protected by a ceramic cap. The typical temperature curve of burning is shown in Fig. 1. The burning

includes two stages. The temperature of a sample at the first stage does not exceed 1200°q (red glow). In accordance with the proposed mechanism of burning, the low-temperature stage involves oxidation of aluminum SFP to γ - Al_2O_3 [reaction (1)]:



with release of energy and products needed for the second (high-temperature) stage to come. During this second stage of burning the gas-phase aluminum suboxides produced in reaction (2) react in the gas phase with the air nitrogen activated by high temperature. In this reaction the aluminum nitride is formed [reaction (3)], which is not further oxidized. The temperature of a sample at the second stage achieves 2400°q (white glow).

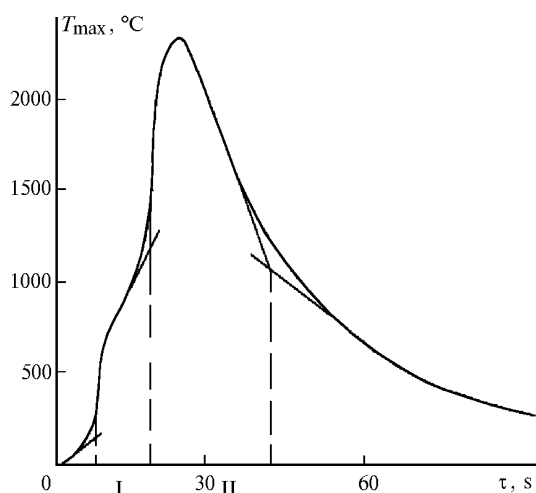


Fig. 1. Typical time dependence of the temperature of burning of aluminum SFP aerogel (stages I and II).

X-ray analysis of burning products has shown that they contain up to 50% of aluminum nitride. This is also supported by the analysis for fixed nitrogen by the Kjeldahl method. The content of fixed nitrogen in the burning products of Al SFP aerogels reaches 17% (Ref. 7). The data of electron microscopy of burning products confirm the assumption on formation of nitrides from the gas phase. Spherical particles of the initial powder after burning completely lose their morphology: burning products constitute a porous structure consisting of needle-shaped crystallites of micron and submicron size. Thus, in contrast to metals, the size of whose particles is more than 1 μm , the process of burning of SFP aerogels can be classified neither as diffusion nor filtration mechanism. Formation of the gas phase of resulting needle-shaped products most likely comes from the gas phase [reactions (2) and (3)].

Besides, we have studied the effect of different agents on the process and products of burning of Al SFP aerogels. The peculiarities of aerogel burning

under conditions of limited air income have also been analyzed.

The effect of different agents has been considered for the superfine powders of Cu, Ni, Fe, Sn, W, Mo, Si, C, B each in the amount of 9% of mass. Adding Cu, Ni, Si, C powders practically does not influence the content of fixed nitrogen from air in the burning products. For the case of tin, the content of nitrogen almost halved. In the presence of Fe, W, and Mo the nitrogen content increases and achieves the maximum (16.6%) in the case of Mo. The temperature of burning of aluminum SFP in the presence of molybdenum addition was maximum and made up about 2400°q.

Among all additions, the agent of our choice was boron being a commonly used component of composite materials. To determine the influence of boron on formation of nitrides, we have studied the effect of the boron SFP addition in a wide range of concentrations (up to 30% of mass at a fixed weighted quantity of 4 g). As the boron content increases, the maximum temperature first increases and then decreases having the peak at the boron content of 15–20%. The content of the AlN phase in the resulting burning products varies similarly. It should be noted that boron nitride and oxides were not found in the burning products by the method of X-ray analysis, what is likely due to their X-ray amorphism.

The peculiarities of burning of different weighted quantities from 0.5 to 15 g were studied using the mixture of Al SFP and 15% of boron. The process of burning of weighted quantities less than 0.5 g consists of one stage with trace amounts of fixed nitrogen in resulting products. As the weighted quantity increases up to 4 g, the maximum temperature increases fast. For large weighted quantities (starting from 8 g) the temperature growth slows down. The dependence of AlN content is similar to the dependence of temperature on the weighted quantity. The highest content of fixed nitrogen (15.3% of mass) corresponds to the maximum weighted quantity (15 g) of the initial mixture (Fig. 2). It should be noted that the percentage of fixed nitrogen in the weighted quantity did not reach maximum under conditions of our experiment.

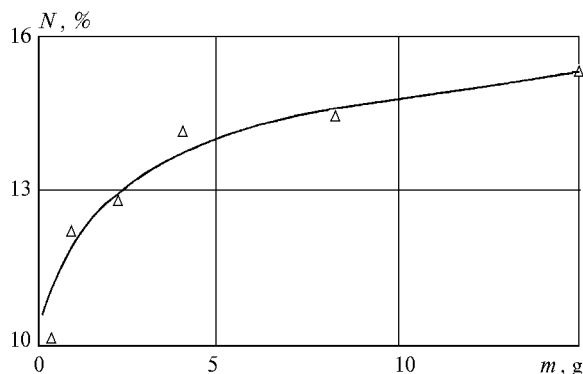


Fig. 2. Content of the fixed nitrogen in the burning products of the (Al + 15% b) SFP mixture aerogel versus the weighted quantity.

Under conditions of limited air income the intensity of nitrogen fixation increases. Burning of Al SFP aerogels in a constant-pressure bomb with volume of 1.43 liter has shown that content of AlN in the burning products increases by more than 20% at the initial weighted quantity of 2 g according to the results of X-ray analysis.

The performed studies of aerogels allow the following conclusions:

- low temperature at the beginning of oxidation and ignition of aluminum and mixture aerogels is indicative of low, not typical for metals in the massive state, thermal conductivity of the system "superfine powder - gas";

- burning of metal SFP aerogels in air is accompanied by formation and incomplete oxidation of nitride phases: fixation of nitrogen from air takes place (up to 50% of mass of aluminum nitride);

- burning of aerosols consists of two phases with formation of intermediate products in the gas phase;

- various additions affect the process of burning and the composition of burning products;

- at the limited air income the burning process also consists of two stages, and the content of fixed

nitrogen in the burning products increases by 20% in terms of aluminum nitride.

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