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# LOW TEMPERATURE SINTERING OF ELECTROEXPLOSIVE NANOPOWDERS

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*By means of the methods of conductivity measurement and transmitting electron microscopy of sintered metal layer it has been shown that electroexplosive coppper and zink powders are sintered with the formation of strong aggregates of corresponding compact metals. It has been also shown that sels-sintereing is a cause of below reduction of metal powder particle size obtained by the method of semiconductor electrical explosion.*

## Introduction

A natural property of metallic nanopowders is a heightened reactivity and, in particular, sintering ability. It is explained by their great specific surface and, probably, by the excess of energy [1–7]. Usually the activity of powders decreases due to formation of surface films (oxides, hydroxides, carbides, carbonates formed, e.g. owing to oxidation of metal surface and absorbed films of carbons and other substances) [8–13]. It is of prime importance for all practical applications of nanopowders at their storage, transportation and compacting as well as at powder production, as self-sintering can reduce their disparity. In this connection by powder thermal stability their ability to be in unchangeable state under usual conditions or when heating up to a definite temperature is implied. The main factors affecting these characteristics are nature of metal, atmosphere composition where the powders are produced and kept, time and temperature of powder storage, the way of producing powder.

The simplest and most common way of stabilizing powders is their passivation by a reactive gas. In practice passivation, as a rule, is made by slow flooding into a volume with a powder of dry air, the protective function being fulfilled a formed thin film of metal oxide.

According to the classical conception [1, 11] and taking into consideration the presence of films the process of sintering can be divided into a number of main stages which are identified by the methods of dilatometry, electrical conductivity, scanning electron microscopy and programming thermal [10–13]:

- compacting by «shaking» without change in size and form of initial particles, the growth of contact area taking place;
- formation and thickening of necks due to grain-boundary diffusion;
- formation and decomposition of surface compounds;
- fusion of metallic nuclei and their coalescence.

These stages become apparent in this or that degree and can be partially or totally divided when studying sintering under the condition of linear (or any other programmed) heating.

In the present work new data on investigation of sintering of electroexplosive (EE) Zn and Cu nanopowders have been presented. The methods of translucent electron microscopy and that of measurement of metal layer conductivity have been used. To determine the reasons controlling the particle distribution into minimal sizes the obtained data have been compared with that from the literature.

## Methods of the experiment

The nanopowders are obtained in the installation described before [16], at the energy content $E/E_s$=2,1...2,2 ($E$ – electrical energy introduced into a conductor, $E_s$ – metal sublimation energy) in the argon atmosphere at pressure 200 kPa; in some experiments oxygen is added to it. The installation permits to cool the working zone up to 268...273 K. The passivation of powders is carried out by means of slow flooding of dry air.

The distribution of particles by size is defined by translucent electron microscopy (the device JEM-100CXII). When carrying out this investigation particle mobility with respect to each other has been tested. For this purpose an electronic beam is focused on the substrate and particle displacement caused by its deformation is observed. While preparing the samples of electroexplosive zinc powder the ultrasonic treatment of alcohol suspension of 10 ml volume at frequency 27 kHz is used.

The distribution of metal particles by size is made by means of size definition not less than 3000 particles and by construction of bar graphs of these data. The average number $a(n)$, average mass $a(m)$ and average surface $a(s)$ particle sizes are defined.

The measurement of electrical conductivity is carried out on direct current at voltage 12 W using a ceramic measuring loop with platinum electrodes. The distance between electrodes is 5 sm. The layer size is 5×2×0,2 sm, the layer density 0,2...0,25 of the compact metal density. The measurement is carried out when heating of the compacting layer of copper and zinc powders in argon current, at linear velocity of temperature raise 20 deg./min in the temperature range 300...600 K.

## Results of the experiment and discussion

The investigation of Zn powders obtained in the experiments on cooling working gas shows that there are separate particles having a unit construction (fig. 1) consisting of units of ~10...30 nm in them. Previously such picture was observed while obtaining aluminium powders at the temperature of working gas (argon) 268...293 K [14].

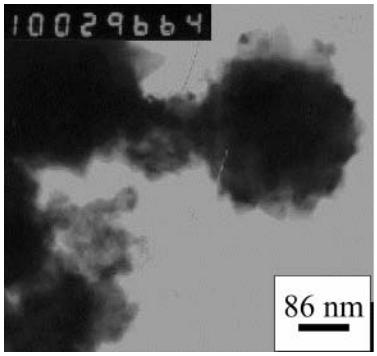
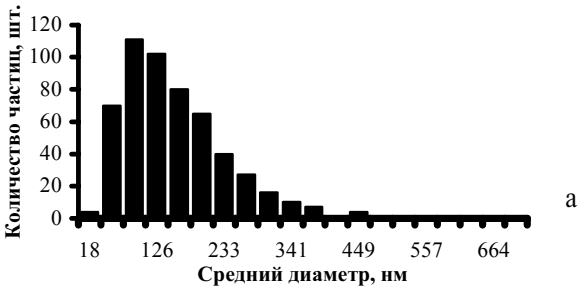



***Fig. 1.*** *The picture of zinc particles*

The analysis shows that in the zinc powders obtained the particles form unstable agglomerates (Fig. 2, *b*).



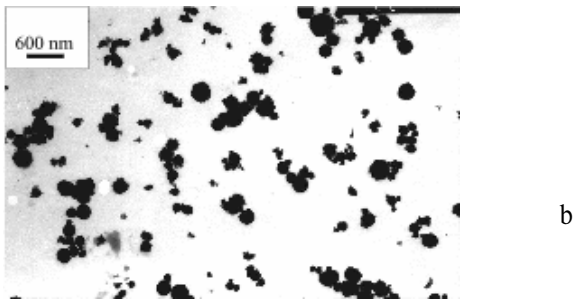
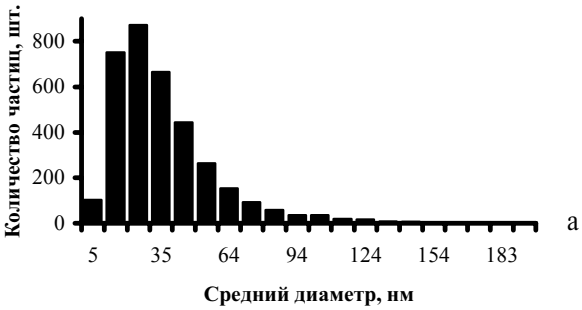




***Fig. 2.*** *The distribution of particles by size (a) and characteristic photomicrography (b) of the agglomerates of zinc powder. Characteristic sizes of particles a(n): 154, 252, 200 nm*

Ultrasonic treatment of zinc powder by alcohol suspension results in destruction of agglomerates shown in fig. 2 and in formation of dispersed system (fig. 3).

In fig. 4 the data on electric resistance of sintering zinc and copper powders are presented. Characteristic temperatures of the beginning of sintering for zinc and copper nanopowders amount to 293 and 373...394 K, correspondingly. In this case, some increase of the layer resistance in the range of 333...363 K is observed for copper powder. It is likely to be explained by partial oxidation of the particle surface by oxygen admixture in argon or by emission of slightly absorbed gas in this temperature range and, as a consequence, «shaking» of metal particles and decrease of interparticle contacts [11, 12].

According to the data of electron-microscopic investigation the initial particles of copper powder obtained in argon have spheric form with average number of size nearly 100 nm (fig. 5, *a*). During the investigation of initial powder it is found out that under the action of electron microscope beam on the substrate and its deformation the majority of particles move independently. In the powder there are only a small number of aggregates that agrees with the results of sediment analysis [8]. Taking into consideration the data of measuring the dependence of Cu powder conductivity, the copper powder structure is investigated after heating up to this temperature.



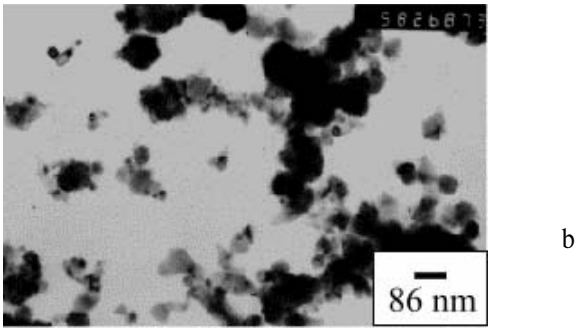




***Fig. 3.*** *The distribution by size (a) and characteristic photomicrography (b) of zinc powder particles after its treatment by ultrasound in ethyl alcohol. Characteristic sizes of particles a(n): 36, 72, 52 nm*

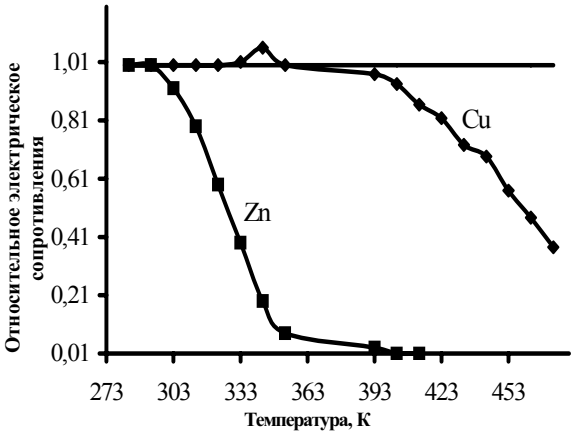



***Fig. 4.*** *The change of relative resistance in sintering metal powders (linear heating is 20 deg/min)*

In fig. 5, *b*, it is seen that after heating the powder the number of thickening necks as well as the decrease of the number of the finest particles. In this case the particles appear to be so tightly adherent that at deformation the substrates move as a single whole. Thus, one can conclude that current contacts which are formed even at temperature 373 K, i. e. nearly 30 % of $T_{melt}$ according to the data of measurements present sufficiently thick and strong necks between the particles.

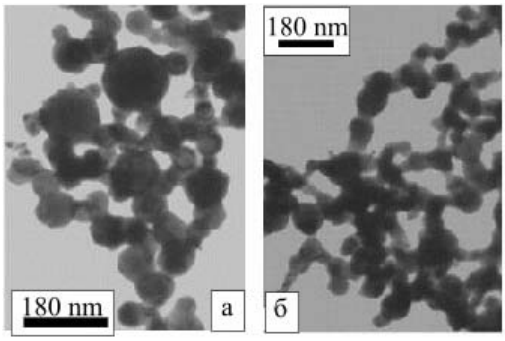



***Fig. 5.*** *The picture of copper particles: a) initial and б) subjected to thermal treatment at 373 K*

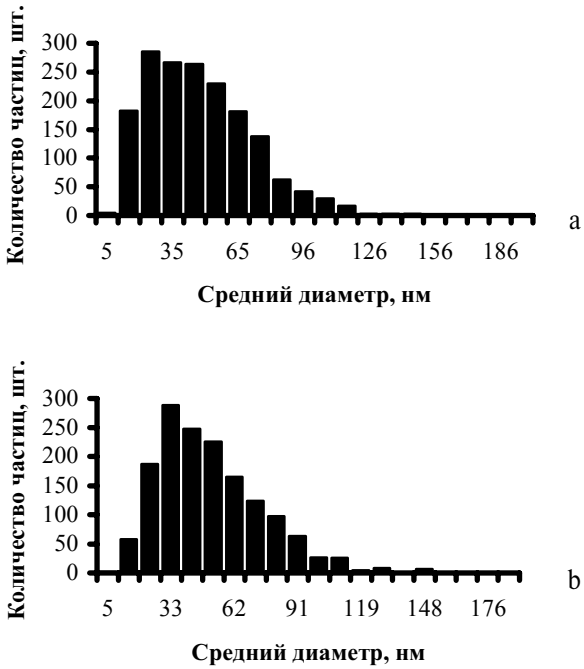



***Fig. 6.*** *The distribution of copper particles by size. Sample: a) initial; b) thermally treated at 373 K*

From the bar graphs it also follows that powder heating up to that temperature results in notable decrease of the number of particles with the size <30 nm. It can be the result of both fusion of fine particles with their subsequent coalescence and that of sintering fine particles with coarse ones and with each other. In this connection one might mention that in the work [17] by measuring specific surface of copper powders obtained by thermal dispersion in the inert atmosphere ( average size if the particles is 75 nm) at different temperatures the sharp decrease of this square even at 300 K was shown, it being understood as a beginning of sintering. On the other hand, from the other experimental data it is known (see, e.g. [4]) that the melting temperature of metal of the particles with size 10...20 nm decreases only by 25...30 %. Theoretical calculations [1, 5, 6] also predict sufficiently less changes in sintering temperature ($T_{sint}$) with these sizes. In this connection it is interesting to note that at the explosion of conductors of fusible metals (Sn, Zn) in the inert atmosphere without cooling we do not succeed in obtaining powders of average size less that 100 nm by means of increase of electric explosion energy and decrease of conductor diameter as, for example, for copper.

The data presented show that sintering of electroexplosive powders is possible at temperatures sufficiently lower the temperature of compact metal melting, namely at $T_{sint}/T_{melt} \leq 0,3$. Sintering starts with the finest fraction, is accompanied by formation of necks, which are gradually thickening, adhering the particles into a strong aggregate.

The development of the process mentioned can be prevented by the surface films. Thus, in the work [16] it is shown that addition of oxygen into the working inert gas results in formation of surface oxide films, decreases the size of the powder particles. In works [10, 12, 13] by the method of conductivity it is stated that active metal powder sintering (Ti, Zn, Al) in the presence of oxygen traces in the inert atmosphere does not occur for the same reason.

The data obtained indicates that comparatively small (in comparison with the temperature of explosion) decrease of temperature of working gas notably decreases the temperature of powder sintering. Besides, the structure of separate particles (150...200 nm) which are presented in the form of strong and dense enough aggregates consisting of the initial nanoparticles (10...30 nm) is revealed. This result shows that at the early stage of electrical explosion the initial particles of size of the order 10 nm are formed, they unite at the temperature of the order of 300 K.

In this connection one can say that the low boundary of powder dispersity obtained by EEC technology is restricted due to self-sintering. In fact, the gas temperature outside the explosion zone usually amounts to 333 K, so that such metals as Al, Zn, Sn must be partially sintered, if it is not prevented by fast formation of surface oxide (or other) films.

### Conclusions

1. It was stated by the electron-microscopic investigation that in sintering of electroexplosive metal nanopowders at temperature lower than 373 K the relative contant of fine fraction decreases.
2. Lowering the temperature of working inert gas as well as the addition oxygen to it results in decreasing the particle size of the powder formed at electric explosion. Thus, lowering the temperature the structure which can indicate that metal particles present aggregates consisting of initial particles of 10...30 nm size is revealed.
3. From the experiments on the change of resistance and the data of electron microscopy it follows that particle sintering of metal powders, even passivated ones, is possible at the temperatures sufficiently lower (nearly $0,3T_{melt}$), than the temperature of compact metal melting. For metals having relatively low temperature of melting (for example, Al, Zn, Sn) sintering is possible even at the temperatures close to 300 K. This circumstance restricts the particle sizes below when obtaining nanopowders by the method of electrical conductor explosion.

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# HEATING COPPER AND ALUMINIUM NANOPOWDERS IN MIXTURES WITH ALUMINIUM AND SILICON OXIDES IN AIR

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*Oxidation of copper and aluminium nanopowders obtained by the method of electric explosion of wire in mixtures with inorganic oxides at heating has been investigated. It is shown that in the presence of $Al_2O_3$, $SiO_2$ and $MnO_2$ oxidation stability of nanopowders raised, which was testified by the values of oxidation parameters: temperature of oxidation start, oxidation degree and maximum velosity of metal oxidation. Oxidation processes taking place in nanopowders slowed down with increase of oxidation additive content.*

## Introduction

The growth of production and expansion of application fields of different metal nanopowders explain the demand for investigation of their properties [1]. For example, nanodispersed aluminium powders find application in the processes of self-spreading high temperature synthesis [2], pyrotechnics [3], powder metallurgy; copper nanopowders are the part of metal-plating lubricating compositions [4], the composition of furnace charge in production of metal-ceramic and ceramic materials, where their application is conditioned by direct contact with inorganic substances including oxides [2]. Due to heightened reactivity of metal nanopowders their contact with other substances is connected with the danger of uncontrolled ignition. At simultaneous metal oxidation by air oxygen exothermic chemical reactions accompanying by significant heat emission can occur [3]. In this connection the problem of research of metal nanopowders at heating them in mixtures with inorganic oxides is rather urgent. The results of the experiment are necessary for the development of means of extinguishing of nanopowders.

The purpose of the given work is to investigate the oxidation of copper and aluminium nanopowders in mixtures with inorganic oxides when heating.