Threshold Phenomena in Nanopowders

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Abstract – The nature of threshold phenomena observed during oxidation, combustion and sintering of aluminium, copper, ferrum and nickel nanopowders was established. The observed threshold phenomena in metal nanopowders obtained by wire electric explosion are caused by destruction (breakdown) of double electric layer. There was established that breakdown of double electric layer results in removal of limitations on diffusion of oxidizers to metal surface, that leads to sharp increase in speed of reactions.

1. Introduction

A threshold phenomenon is an extreme change in one of the parameters of a system with a relatively moderate change of another parameter. Nanopowders belong to the systems in a metastable state. Under definite conditions (temperature, pressure, ultrasound treatment etc.), such a state can relax in the more stable metastable state or in the stable one. In case of metal nanopowders, an excess energy releases in the form of heat or radiation. For the oxidation processes, the stored energy is a constituent of the thermal effect. The increase in particle sizes leads to the increase in specific surface area (S_{sp}) which is the parameter of the rate equation for a heterogeneous chemical reaction:

$$v = k \cdot S_{PS} \cdot [A_{gas}], \qquad (1)$$

where k is the constant of the chemical reaction rate; $[A_{gas}]$ is the concentration of the gaseous component.

When the diameter is changing from 1 to 0.1 μm, a sharp variation in properties of powders is observed. For instant, the apparent density of the powder decreases by a factor 4—10, and other properties are also changing.

The objective of the present work was to establish the nature of threshold phenomena observed during oxidation, combustion and sintering of metal nanopowders.

It is assumed that the increase in particle sized of metals leads to deceleration of the thermodynamically permitted oxidation process. It does not occur due to the limitation of oxidizer diffusion through the layer of products. In fact, it is realized because of an electric field between the negatively charged surface and the positively charged sub-layers at the boundary metal-oxide (hydroxide) [1].

2. Experimental approach

The powders were produced by electrical explosions of wires. The explosions were carried out in argon at a pressure of $1.5 \cdot 10^5$ Pa in the machine which is schematically shown in Fig.1. A 0.3 mm wire was used as an exploded conductor. The size and the shape of the particles were measured using a scanning electron microscope JSM-840 (JEOL). The sintering of compacted samples of copper and silver nanopowders was carried out in argon and in vacuum (10^{-4} mm of mercury) in a strip heater of a vacuum post VUP-4. Oxidation processes of the nanopowders were studied by means of differential thermal analysis using a thermoanalyzer SDT Q600.

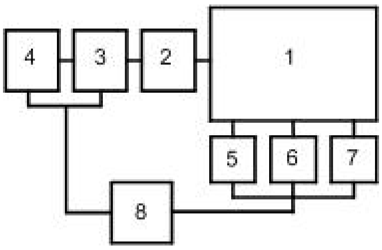

Fig. 1. Structural scheme of the experimental setup. 1 — explosion chamber with a wire feeding mechanism; 2 — discharger; 3 — capacity storage; 4 — charger; 5 — vacuum system; 6 — gas filling system; 7 — system for separation of explosion products from gas; 8 — control panel

3. Experiment

When sintered the silver nanopowders in vacuum at 60 °C in the heater, a planar heat wave was propagating through the sample. The sample (tablet) was shining during several seconds. The maximal temperature was 1600 °C. The sample mass did not change. When the compaction pressure was increased from 1000 to 3000 N/cm², the onset temperature of sintering decreased to 27 °C. The sintering of compacted copper samples was carried out in high purity argon with additional cleaning by heated copper powder. For one of the exothermal effects, no mass variation was detected during heating whereas the heat released. It is related to relaxation processes.

According to the differential thermal analysis data, the oxidation of the nanopowders under the conditions of threshold phenomena occurs during heating in air (fig. 2, *a*, *b*).

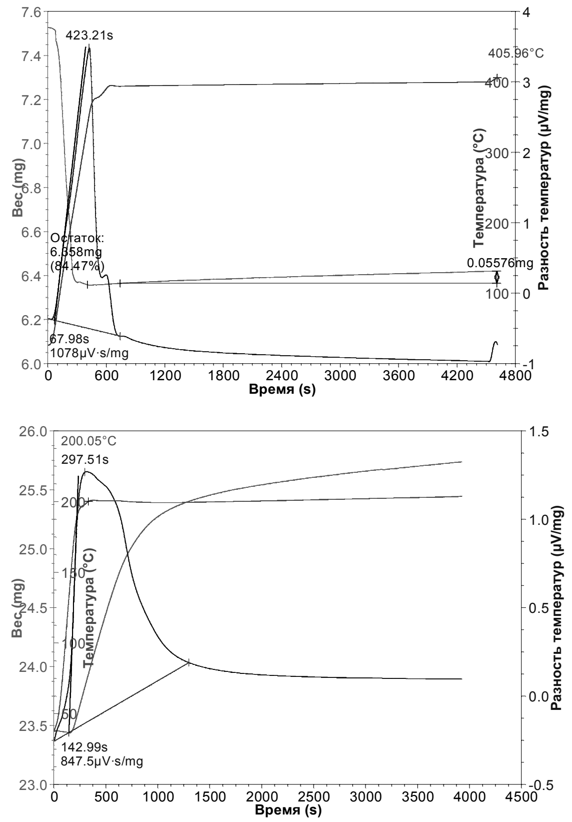

Fig. 2. Thermograms of the nanopowder samples: a) aluminium, m=5 mg, in nitrogen; b) copper, m=7 mg, in air

4. Results and Discussion

According to the obtained experimental results, the heat release rate during heating in vacuum in the narrow range of temperature (7 °C for Ag nanopowder and 8 °C for Cu nanopowder) increases by a factor of 40 and 30, respectively. Silver oxide Ag_2O is stable up to 180 °C, i.e., at $T \geq 180$ °C $\Delta G^{\circ} > 0$ and the interaction with oxygen is not thermodynamically permitted. Thermal effects of cupper oxidation into Cu_2O are enough low CuO to ensure a high temperature in a heat wave during sintering. During heating in vacuum up to a definite threshold temperature, sel-heating during sintering of nanopowders is possible only due to relaxation processes in surface and sub-layers. While electric explosion nanoparticles during dispersion and cooling pass through a liquid-phase condition stage and undergo strong Laplace compression, as a result of which all linear and volumetric defects are pushed out on surface of particles. At the same time, there is a formation of layered structure of surface and near-surface layers: near-liquid particles are positively charged due to thermoemission of electrons, and near-gaseous phase of wire electric explosion products – negatively. According to dynamics of particles dispersion, while cooling there is a condensation of near-gaseous phase on surface of near-liquid one and fast cooling and hardening of substance from surface of a particle to its inside. During slow oxidation and diffusion of an oxidizer, which are protons (H^+), the double electric layer is transformed and remained. Thus, the impurity contained in a wire can concentrate in surface and near-surface layers or in the central part of nanoparticles [2]. Modes of nanopowders obtaining by wire electric explosion have a certain importance for concentration of impurities. For aluminium (fig. 3), which is a light element, there could be observed concentration of impurities in near-surface layer: basically there are iron, manganese, copper and their compounds (a dark layer), which cause ferrimagnetic properties of nanopowders [3], amplified with the Kondo effect.

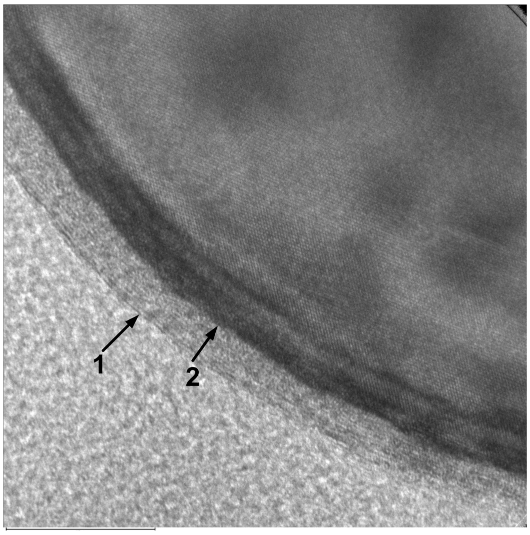

Fig. 3. Microphotography of an aluminium particle: 1 – oxide – hydroxide layer (Al_2O_3, Al $(OH)_3$); 2 – layer enriched with impurities of heavy metals

Both metals and their compounds are more refractory, than aluminium, therefore, probably, at first impurities transform to a firm condition, setting form and sizes of particles. Presence of significant part of impurities in surface of aluminium and copper particles is confirmed with the data of x-ray photoelectronic spectroscopy. Contribution of impurities multi-charged ions promotes creation of a steady double electric layer.

Table 1. Activity parameters for different metal nanopowders

Type of nanopowder	Oxidation start temperature*, °C	Maximal speed of oxidation, $\Delta m/\Delta\tau$, mg/s	$\Delta H/\Delta m$, rel.unit	Oxidation rate at heating up to 800, %
Al	420	0,19	4,6	33,7
Cu	120	0,05	1,6	20,3
Fe	180	0,09	2,1	14,1
Ni	310	0,07	1,7	12,4

* – start of oxidation is a deviation of TG from horizontal position

According to the thermal analysis at achievement of threshold temperatures weight, oxidation speed, and thermal emission (fig. 2) grow rapidly.

The results of thermal analysis of copper nanopowders samples series are given in the table 2.

Table 2. Characteristics of copper nanopowders obtained by wire electric explosion

Sample	Specific surface area, m^2/g	Oxidation start temperature, °C	Mass growth according to TG, % mass. (up to 800 °C)	Modified thermal effect ($S/\Delta m$), rel.unit
Cu30	6.2±0.2	165	20.1	1.53
Cu28	8.2±0.2	170	19.4	1.43
Cu26	10.2±0.3	170	19.6	1.62
Cu24	5.7±0.2	160	18.7	1.54
Cu22	3.8±0.2	170	19.8	1.52
Cu20	3.7±0.3	170	20.8	1.41
Cu18	3.9±0.1	170	20.6	1.24

It is necessary to note, that for nanopowders with particles diameter reduction the thickness of oxide – hydroxide covering decreases for a range of 30–200 nanometers, and at further reduction metal particles are completely oxidized. Presence of double electric layer and its breakdown at heating is proved by independence of oxidation start temperature from metal particles diameter.

5. Conclusions

1. The observable threshold phenomena in metal nanopowders obtained by wire electric explosion are caused by destruction (breakdown) of double electric layer, formed in irreversible proceeding processes at electric explosion and chemical oxidation-reduction processes at passivation.
2. Breakdown of double electric layer results in removal of limitations on diffusion of oxidizers to metal surface that leads to sharp increase in speed of reactions. Thus, for nanopowders series, obtained by wire electric explosion, the oxidation start temperature does not depend on diameter of particles in a range of 30–200 nanometers.

References

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