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PASSIVATION OF METAL NANOPOWDERS OBTAINED BY ELECTRIC EXPLOSION OF SEMICONDUCTORS

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The influence of composition and gas flow rate at passivation on content of unoxidized metal, particle size and temperature on the metal nanopowder layer obtained by the method of semiconductor electric explosion has been studied. It is shown that the time of forced passivation can be tens times less in comparison with passivation at spontaneous gas diffusion in powder layer.

1. Introduction

Storage and use of metal nanopowders cause a number of specific problems, connected with their high activity. Finely dispersed powders oxidize appreciably at their contact with air. Heat released in the process of oxidation without sufficient heat removal (powders in freely poured condition have a low heat conductivity) may result in metal self-heating and further sintering or powder inflammation.

All stated processes are inherent to full extent in metal nanopowders, produced by the method of electric explosion of conductors (EEC). As the investigations of the process of presintering show [1], the initial sintering temperature of some EEC conforms to ~30 °C. Therefore, it is urgent to ascertain the regularities of passivation process, allowing for decrease of the passivation time and determination of its optimal parameters for storage powders properties (amount of active metal).

On the other hand, the importance of the problems, connected with powder passivation by means of just oxygen containing atmosphere, is defined by the fact that the significant part of existing techniques of metal powder recycling is meant for a definite (usually not large) content of oxide phases.

Change in properties of Cu and Ni powders with average number particle size of 60 nm at their air storage is studied in the paper [2]. It was stated that nickel powders oxidation process lasts 90...100 days, and copper oxidation process lasts 280 days. According to the data of the paper [3], powder apparent density obtained by the method of EEC increases at their storage as the result of desorption and oxidation processes, attaining constant value in ~100 days. In the paper [4] it is shown that the process of aluminium powders oxidation proceeds during ~12 days.

The aim of the given paper is the investigation of the influence of gas mixture flow rate, as well as oxygen and water vapors concentration in gas on nanopowder oxidation that is necessary for the development of methods of passivation time decrease.

2. Experimental technique

Production of nanopowders by the method of EEC to decrease their activity the spontaneous passivation by air is usually applied – see, for example [3–6]. In this case, a container with nanopowder, obtained in the atmosphere Ar, is filled through a small regulated hole spontaneously with air, which diffuses through the layer of argon, being over the powder, and then into the layer

of powder. Air oxygen interacts with the powder and forms oxide layer on the surface of the particles, which restricts further metal oxidation. For the portion of electric explosion powder Al (EEP-Al) with weight ~0,5 kg the process of passivation (appreciable oxidation) lasts about 3 days. In this case, the content of metal Al in the powder decreases to 82...92 %. At passivation process acceleration by means of growth of air access the powder self-ignition may occur. It is stated that powder temperature, measured in the middle of the layer in the process of such passivation, should not exceed 50 °C, for it to stay nanodispersed [3].

To investigate the process of forced passivation another installation was used, Fig. 1.
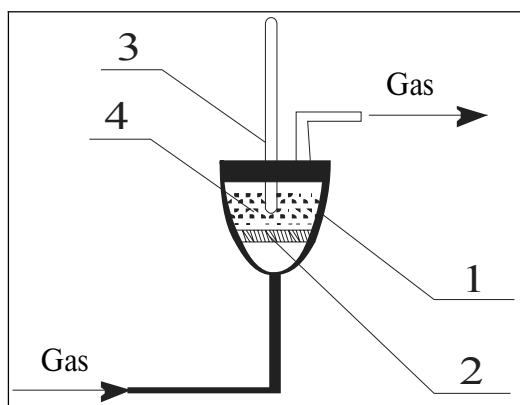
Fig. 1. *Scheme of installation for powder oxidation study*

Powder was placed in reaction vessel − 1 (volume 25 ml, powder weight 1,75 g) in inert atmosphere. The vessel had porous bottom − 2, through which gas mixtures (O_2+Ar, Ar+H_2O, O_2+Ar+H_2O) were fed at a certain velocity. In the course of blasting, powder temperature in the layer − 4 was controlled by the thermocouple − 3. At low velocity of heat removal the temperature in the layer T was proportional to the part of oxidized metal, and the oxidation rate was proportional to dT/dt, where t is the time.

Raw, nonpassivate powder of Al, which was obtained in argon atmosphere at $E/E_s \approx 2$, $P=1 \cdot 10^5$ Pa, $d_0=0,3 \cdot 10^{-3}$ m (here E and E_s is the energy introduced into conductor at EEC, and standard energy of metal sublimation, d_0 is the diameter of the conductor) was used in the experiments. All procedures were carried out in argon atmosphere in a hermetic box. The content of unoxidized metal in the samples was determined by volumetric technique by hydrogen extraction at dissolving a portion of powder in alkali, after a certain time of its passivation. The investigations of the samples by the method of electron microscopy were carried out at transparent electron microscope JEM-100 SHP.

3. Results and discussion

The curves of temperature change $T(t)$ are shown in Fig. 2 and 3. It follows from the diagrams that temperature values pass through the maximum. The value and position of maximum depend on blasting rate and O_2 concentration in Ar. The growth of O_2 concentration and the rate of gas flow increase the magnitude of maximal temperature and shift its maximum to the coordinate axis. The initial rate of particle oxidation with exposed surface should be maximal at $t=0$. The presence of maximum at the initial area of reaction is determined by heat losses into environment and powder heating and O_2 diffusion to powder particle surface that is connected with its agglomeration and presence of adsorbed gases on particle surface.

Dependence of unoxidized metal content in (ωAl) powder on the process parameters is presented in Fig. 4. It is seen that the initial maximum of rate falls on $t=0$ at any gas rates and concentrations, that is connected with intermittent character of the experiment and insufficiently often sampling at the beginning of the experiment. It follows from the comparison of curves 1 and 2 (Fig.4) that current and final content of active aluminium does not practically depend on the rate (V) of gas flow at $V \geq 50$ ml/min. However, it follows from Fig. 5 that at the given oxygen concentration the growth of gas flow rate results in fast decrease of the final ($t > 30$ min) content of active aluminium in the powder in the range of $V < 50...60$ ml/min; at further increase of flow rate the level of powder oxidation stays constant.
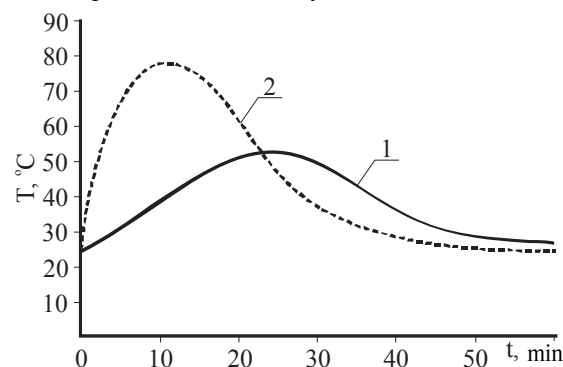

Fig. 2. *Dependence of sample temperature at its passivation in the mixture of Ar+O_2 on the time and concentration of oxygen: 1) 2,5; 2) 5 vol. %. Gas flow rate is V=50 ml/min in both cases*
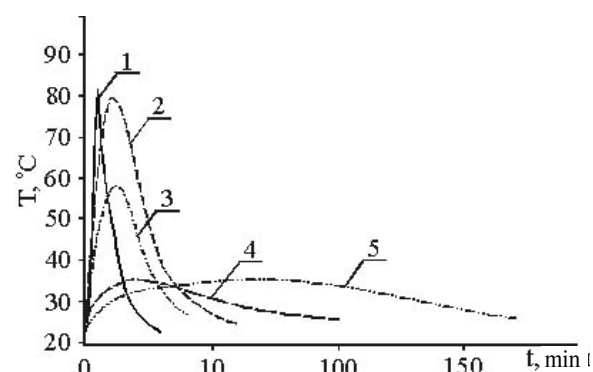

Fig. 3. *Dependence of temperature of aluminium powder on passivation time and on the rate of gases mixture flow: 1) 100; 2) 50; 3) 25; 4) 10; 5) 5 ml/min. O_2 concentration was 5 vol. % in all the experiments*

It is known from scientific literature that the process of oxidation occurs more intensively at metal contact with water vapors than at their interaction with oxygen (see, for example [5]). It was important to study water vapor influence on passivation process as there is always a deal of moisture in the air at the real conditions of pas-

sivation. Water vapors were produced by argon bleeding through the tube with porous material, soaked with water by moisture capacity. Relative humidity of argon (or the mixtures of O_2+Ar with water vapors) was supported on the level of 93 % at $T = 20$ ℃.
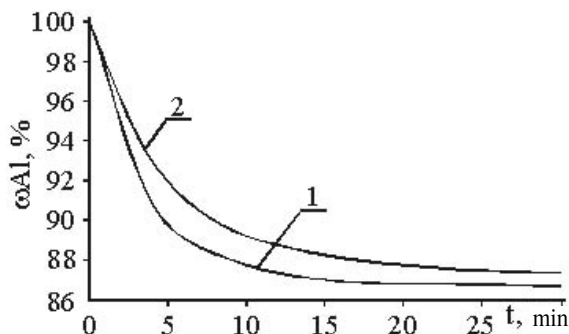

Fig. 4. *Change of metal aluminium content in EEC of Al at its passivation for different rates of gas flow: 1) 100; 2) 50 ml/min. Oxygen concentration is 5 vol. % in both cases*
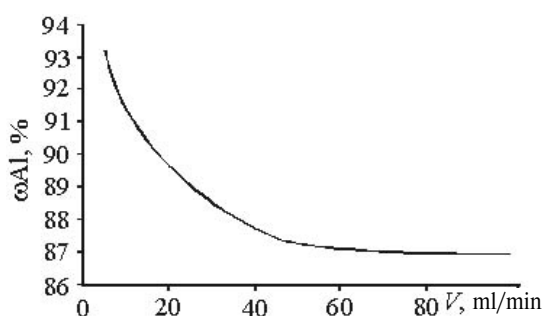

Fig. 5. *Dependence of metal aluminium content in EEC of Al on the rate of mixture (Ar+O_2) flow after the process of passivation (t=30 min). O_2 concentration in gas mixture is 5 vol. %*

Change of samples temperature depending on passivation time at different compositions of gas mixture is shown in Fig. 6.
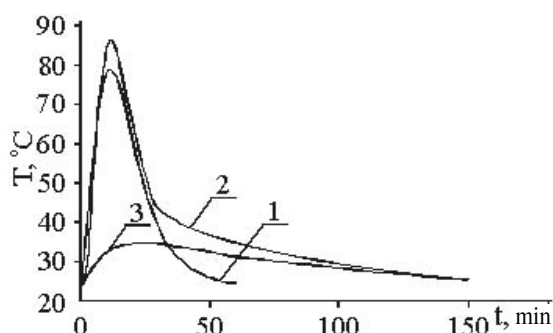
Fig. 6. *Temperature dependence of EEC samples of Al on passivation time and gas mixture composition: 1) O_2 content in argon is 5 vol. %, without H_2O vapors; 2) O_2 content in argon is 5 vol. % with H_2O vapors; 3) Ar+H_2O vapors. The rate of gas mixture in all cases is 50 ml/min*

It follows from the obtained data that samples peak temperature at passivation with oxygen containing mixture is significantly higher than at passivation with argon, containing only water vapors. It may be connected specifically with the fact that standard enthalpy of the

reaction in the first case is approximately two times larger than in the second one (~830 and 415 кJ/mole per an atom of Al [7]). It may be also connected with different state of surface layers: thin oxide and hydroxide layers on the surface of aluminium particles probably differ considerably in heir physicochemical properties.

Presence of moisture in oxygen containing mixture results in a certain intensification of oxidation processes that is indicated by magnitude of peak temperature on the curve 2, Fig. 6. Besides, the rate of oxidation in the presence of water vapors decreases slower that indicates higher permeability of aluminium oxohydroxide film in comparison with the oxide one. Form of the curve 2, Fig. 6, indicates obviously the complex structure of oxidation process, in which both oxygen and water vapors participate, and the dependence 2 itself, is probably the sum of processes, described by the curves 1 and 3, Fig. 6. On the basis of the rate of temperature change, $(\Delta T/\Delta t)O_2$=0,04 K/s, $(\Delta T/\Delta t)_{H_2O}$=0,06 K/s, and duration of oxidation process to the maximum of the curves 1 and 3, it is possible to conclude that at the first stage the powder interacts generally with oxygen, at the second one it interacts with water vapors. Therefore, the layer of hydroxide should be under the layer of oxide which is confirmed by the data about the structure of surface layers of aluminium particle, given in [8]. The supposed order of surface oxidation may be explained by the fact that (*a*) oxygen concentration is higher than the same of water vapors, (*b*) oxygen is more active in reactions than water, and (*c*) the coefficient of water diffusion in oxide lattices is higher than the coefficient of O_2 molecules, as the size of water molecule is less and their ionic dissociation occurs easier.

In the experimental conditions the influence of rate of mixture Ar+H_2O flow on powder temperature is marked weaker, than at passivation with oxygen containing mixture (Fig. 3 and 7). Probably it is also explained by the fact that diffusion coefficients of water vapors in gas flow and through the film are higher than the coefficients of O_2 molecules that decreases the influence of diffuse stage on oxidation process.

At the initial stage of the process the content of aluminium in the sample passivated in Ar+H_2O medium is slightly lower than at passivation with oxygen containing mixture, though this difference is insignificant. At time equal to 5 minute, the content of metal aluminium was 89,7 % at passivation with water vapors, at passivation with oxygen containing mixture it was 91,8 % that is probably explained by higher permeability of oxohydroxide film in comparison with oxide.
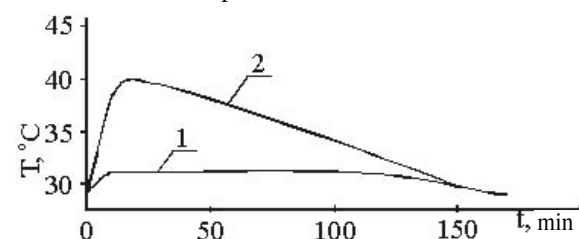

Fig. 7. *Temperature dependence of the EEC layer of Al on the time for different rates of mixture Ar+H_2O flow: 1) 5, 2) 50 ml/min*

It should be noted that these preparations differed only in initial conditions of passivation (first 100 min), further storage and preparation was carried out on the air. That is, the quality of the powder is generally determined by the initial conditions of passivation. It is important that the blasting passivation is more reliably controlled, and time required for it is tens times less than at spontaneous inleakage of air.

Conclusions

1. It is shown experimentally that at passivation of Al, Zn nanopowders by puffing of oxygen containing gas mixtures temperature change may be rather high to result in particles sintering, especially of low-melting metals (aluminium, zinc) powders and powders quality loss: increase of degree of particles agglomeration, their size enlargement.

2. Water vapors presence in oxygen containing gas mixture intensifies the oxidation process of Al EEC and increases its duration and depth that is connected with higher diffusibility of water molecules, in comparison with the same of O_2, and increased diffused permeability of oxohydroxide films.

3. The amount of free metal remained after passivation in the powder is defined both by oxidizer concentration (oxygen, water vapors) in argon, and the rate of gas flow through the sample. It is connected with temperature rise and correspondingly diffused permeability of formed oxohydroxide film.

4. At forced passivation of nanopowders with gas mixtures the process time may be reduced in tens of times in comparison with spontaneous passivation. To prevent self-heating it is necessary to use vitiated (to 2,5 %) mixtures with argon.

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