Literature

1. Geguzin Ya.J. Physics of sintering. – Moscow: Nauka, 1984. – 312 p.
2. Andriyevskiy R.A. Powder material science. – Moscow: Metallurgia, 1991. – 205 p.
3. Skorokhod V.V., Solonin S.M. Physico-metallurgical bases of sintering powders. – Moscow: Metallurgia, 1984. – 159 p.
4. Buffat Ph., Borel J.P. Size Effect of the Melting Temperature of Gold Particles // Phys. Rev. – 1976. – V. A13. – № 4. – P. 2287–2292.
5. Alymov M.I., Maltina E.I., Stepanov Y.N. Model of Initial Stage of Ultrafine Metal Powder Sintering // Nanostructured Mater. – 1994. – V. 4. – № 6. – P. 737–742.
6. Alymov M.I., Semichev S.V. The influence of initial particle size and neck size on its growth at sintering of spherical particles // Physics and chemistry of metal treatment. – 1999. – № 5. – P. 56–60.
7. Savelyev G.G. The mechanism of energy storing at production of metal powders by electroexplosion of conductors. // The 4th scientific-technical conference of Siberian chemical combine: Coll. of reports. Section 1. Production of ultradispersed metal powders and metal oxides. – 28-31 may, 1996. – Seversk, 1996. – P. 12–15.
8. Savelyev G.G., Yurmazova T.A., Lerner M.I., Stepanyan J.V., Tepper F., Kaledin L., Ginly D. Agglomeration and aggregation of electroexplosive metal nanopowders // Physics and chemistry of ultradispersed (nano-) systems: Coll. of scient. papers of the VI All-Russia (International) conf. – Moscow, 2003. – P. 265–269.
9. Savelyev G.G., Galanov A.I., Lerner M.I., Denisenko A.V., Ginly D., Tepper F., Kaledin L. Kinetics of sintering of electroexplosive nanopowders at linear heating // Physics and chemistry of ultradispersed (nano-) systems: Coll. of scient. papers of the VI All-Russia (International) conf. – Moscow, 2003. – P. 349–352.
10. Galanov A.I., Savelyev G.G., Lerner M.I., Denisenko A.V., Ginly D., Tepper F., Kaledin L. Investigation of sintering of electroexplosive metal nanopowders by the methods of conductivity and dilatometry // Physics and chemistry of ultradispersed (nano-) systems: Coll. of scient. papers of the VI All-Russia (International) conf. – Moscow, 2003. – P. 305–309.
11. Geguzin Ya.J. Why and how hollow disappears. – Moscow: Nauka, 1983. – 192 p.
12. Savelyev G.G., Galanov A.I., Lerner M.I. a. o. Sintering of electroexplosive copper nanopowder // Proceedings of Tomsk polytechnic university. – 2004. – V. 307. – № 2. – P. 100–105.
13. Galanov A.I., Savelyev G.G., Lerner M.I. a. o. Peculiarities of electroexplosive nanopowders sintering // Physico-chemical processes in inorganic materials: Coll. of reports. Of the IX International conf. – Kemerovo, 2004. – V. 2. – P. 119–123.
14. Lerner M.I., Shamanskiy V.V. Formation of nanoparticles under the action on metal conductor by current pulse of high power // Journal of structural chemistry. – 2004. – V. 45. – № 1. – P. 112–115.
15. Lerner M.I., Davudovich V.I. Formation of highly dispersed phase at electric explosion of conductors // Production, properties and their application of energy-saturated ultradispersed metal powders and their compounds: Coll. of scient. papers. of All-Russia conf. – Tomsk, 1993. – P. 23–34.
16. Lerner M.I. Operation of the process of high dispersed particle formation in the condition of electric explosion of conductors: Dissert. ... cand. of tech. sciences. – Tomsk, 1988. – 15 p.
17. Troitzkiy V.N., Rakhmatullina A.Z., Berestenko V.I., Gusev S.V. The temperature of beginning of ultradispersed powder sintering // Powder metallurgy. – 1983. – № 1. – P. 13–15.

UDC 541.16:182

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

Yu.A. Amelkovich, A.P. Ilyin, A.Yu. Godymchuk

The Research Institute of High Voltages of Tomsk Polytechnic University
E-mail: amely@tpu.ru

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.

The experiment

In the work aluminium nanopowders (ANP) and copper nanopowders (CNP) obtained by means of electric explosion of wire of diameter 0,3 mm and 60 mm long in the argon medium have been investigated. The given method is based on dispersion of metal conductors by powerful current pulses (up to 500 kA) at the discharge of capacitor battery [5]. The value of the energy introduced into conductor is measured by means of supply of various voltage (from 18 to 30 kW) to the exploding conductor, it amounted from 0,7 to 1,8 of its sublimation energy. The nanopowders were obtained at an experimental-industrial device «UDP-4G» of scientific management group of «The research institute of high voltages at TPU», city Tomsk [6].

Determination of microstructure characteristics of ANP and CNP surfaces was made by means of a scanning electron microscope JSM-840 of «Jeol» (Japan) production.

The square of specific surface (S_{spec}, m^2/g) of nanopowders was measured by BET method using ASAP2020 device. Using the value of the magnitude S_{spec}, the value of average surface diameter (d_{av}, mkm) of powder particles was calculated by empiric formula [7]:

$$D_{av}=6/(\rho S_{spec}),$$

where ρ – metal density, g/sm^3.

As inorganic additives chemically inert aluminium oxide (γ-Al_2O_3) and possible oxidants – silicon (SiO_2) and manganese (MnO_2) oxides were chosen.

To study the influence of the oxides involved on oxidation parameters of nanopowders at heating the unconsolidated mixtures (in freely poured form) containing 90, 50 and 10 % of mass of nanopowders (the method of dry mixture) were prepared. The oxides had been bolted beforehand through the sieve with the meshes of 63 mkm size.

The determination of oxide influence on the oxidation parameters of the nanopowders under investigation was carried out on the basis of the data of differential-thermal (DTA) and thermogravimetric analysis using derivatogrph Q-1500 (Hungary) of «Paulik-Paulik-Erdey» system in the mode of linear heating (10 °C/min) in the air atmosphere in the temperature range 20...900 °C [8].

The nanopowders reactivity was estimated by the following parameters: temperature of oxidation start (t_{os}, °C), oxidation degree (the mass growth of samples due to oxide formation, mas. %), maximum velocity of metal oxidation (the change of sample mass per minute, V_{ox}, mas. %/min) and reduced oxidation heat effect ($S/\Delta m$, rel. unit). The temperature of the beginning of intensive oxidation processes by Piloyan methods [9] was taken as the temperature of oxidation start. The degree of oxidation was defined by thermogravimetric dependence as a relation of mass growth of the sample to initial metallic powder mass in the sample. The maximum velocity of metal oxidation was also defined by TG as the quickest change of sample mass in the definite temperature range (fig. 1).

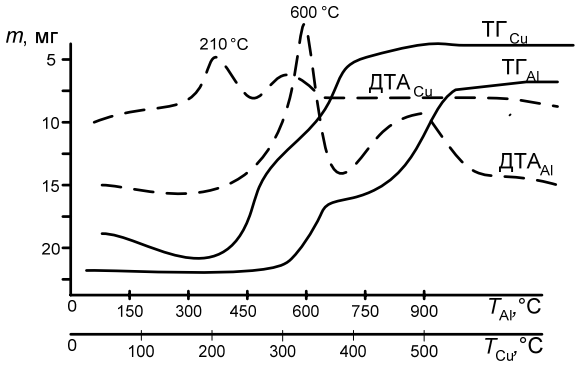


Fig. 1. *Derivatograms of sample oxidation of aluminium and copper nanopowders: TG – change of sample mass in time, mg; $ДТА_{Al}=ANP_{Al}$ and $ДТА_{Cu}=CNP_{Cu}$ – dependence of heat emission during heating; heating speed – 10°C/min, atmosphere-air*

Testing the initial electroexplosive nanopowders of aluminium showed that with the increase of voltage delivered on the conductor the dispersity of particles raised. The change in the temperature of oxidation start on the particle size of nanopowders was observed in the narrow range from 530 to 550 °C (table 1), but it was not more than standard temperature of aluminium melting (660 °C). C The degree of nanopowders oxidation also changed ambiguously. The reduced oxidation heat effect of oxidation processes proceeding in nanopowders had a tendency to increase: the more the square of the specific surface of particles, i.e. the fewer diameters of particles, the higher the reduced heat effect of the reaction.

Table 1. *Characteristics of aluminium nanopowders obtained by means of electric explosion of conductors*

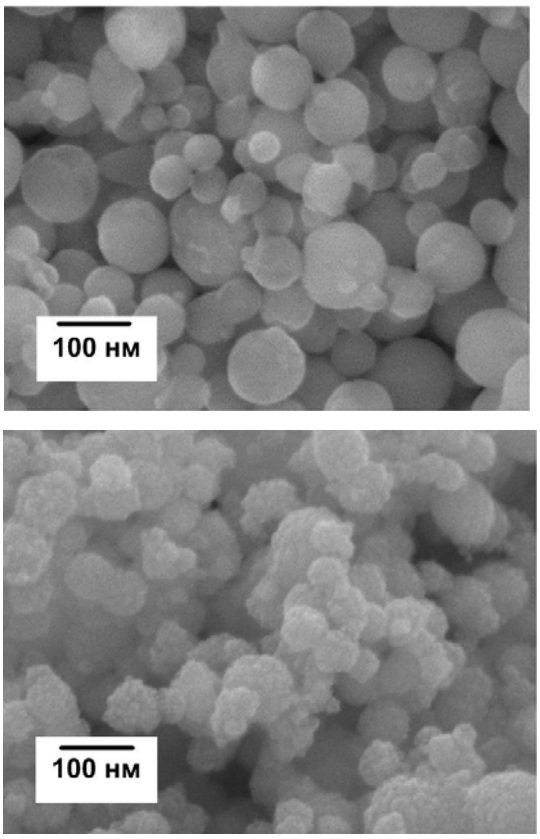
№№ п/п	Voltage delivered to the conductor exploded, kW	Square of specific surface S_{spec}, m^2/g	Temperature of oxidation start T_{os}, °C	Growth of mass according to TG up to 660 °C Δm, mass. %	Reduced heat effect of oxidation ($S/\Delta m$), rel. unit
1	30	10,8±0,3	540	27,4	3,9
2	28	9,9±0,3	530	28,6	5,5
3	26	9,9±0,9	550	26,5	3,7
4	24	9,3±0,3	540	35,4	2,9
5	22	8,8±0,25	550	39,1	3,3
6	20	6,7±0,2	540	31,3	3,1
7	18	7,7±0,25	550	28,3	2,9

Table 2. *Characteristics of copper nanopowders obtained by means of electric explosion of conductors*

№№ п/п	Voltage delivered to the conductor exploded, kW	Square of specific surface S_{spec}, m^2/g	Temperature of oxidation start T_{os}, °C	Growth of mass according to TG up to 660 °C Δm, mass. %	Reduced heat effect of oxidation ($S/\Delta m$), rel. unit
1	30	6,2±0,2	165	20,1	1,53
2	28	8,2±0,2	170	19,4	1,43
3	26	10,2±0,3	170	19,6	1,62
4	24	5,7±0,2	160	18,7	1,54
5	22	3,8±0,2	170	19,8	1,52
6	20	3,7±0,3	170	20,8	1,41
7	18	3,9±0,1	170	20,6	1,24

It is also typical for nanopowders to have constant temperature of oxidation start of the particles exposed to passivation by air, it amounting 160...170 °C (table 2). The degree of oxidation of metallic copper before melting was not more than 20,8 mass %. In this case the reduced heating effect at the copper nanopowders oxidation (table 2, samples 3–7) with the decrease of specific surface square (the increase of particle dispersivity) fell down.

ANP and CNP testing showed that nanopowders particles have a spheric form (fig. 2). For the investigation ANP and CNP were chosen the specific surface square of which amounted 9,9 and 3,7 m^2/g correspondingly.



a

b

Рис. 2. *Microphotos of particle fractions of electroexplosive nanopowders a) aluminium; b) copper*

Results and their discussion

When contacting metal nanopowders with air there forms a layer of oxides preventing from the total oxidation on the metallic particles. Heating up to definite temperatures the oxidation-reduction processes are initiated in the metallic particles [4]:

$$2Al+3/2O_2=Al_2O_3–1675 \text{ kJ/mol},$$

$$Cu+1/2O_2=CuO–157 \text{ kJ/mol},$$

$$2Cu+1/2O_2=Cu_2O–173,2 \text{ kJ/mol}.$$

According to TG (fig. 1), the oxidation processes in ANP become apparent at ~ 500 °C (table. 3, samp. 1), in this case the maximum velocity of oxidation amounts 4,75 mass. % per minute. In linear heating the maximum degree of aluminium transformation (oxidation) amounts 51,8 mass. %.

When heating ANP in mixture with oxides the temperature of aluminium oxidation start increased with the growth of mass content of oxides in the mixture, which appeared to be typical for all types of examined samples [10]. Thus, in the presence of 10 mass. % of aluminium oxide the temperature of oxidation start increased by that time by 20 °C (table 3, samp. 2). In this case the more the additive content (oxide) in mixture, the more maximum speed of aluminium oxidation (table 3, samp. 2–4).

In the presence of silicon oxide in the mixture the temperature of ANP oxidation start also increased, but the velocity of aluminium oxidation changed insignificantly (table 3, samp. 5–7). As it was at introduction of Al_2O_3, heating ANP with SiO_2 was accompanied by less mass growth in comparison with ANP oxidation without additives in the similar conditions: the degree of ANP oxidation decreased from 50,3 to 43,9 mass. % when decreasing the content of aluminium metallic nanopowders in mixture.

Table 3. *Parameters of aluminium nanopowders oxidation in mixtures with aluminium, silicon and manganese (II) oxides*

№	Content	Temperature of oxidation start T_0 (±5), °C	Degree of sample oxidation, Δm* (±2 %), mass. %	Maximum oxidation velocity, V_{ox}, mass %/min	Temperature of finishing intensive oxidation, T_{io}, °C
1	ANP	500	51,8	4,8	810
2	ANP:Al_2O_3=90:10	520	39,6	3,5	590
3	ANP:Al_2O_3=50:50	560	47,1	4,4	590
4	ANP:Al_2O_3=10:90	590	44,7	9,3	600
5	ANP:SiO_2=90:10	520	50,3	4,7	580
6	ANP:SiO_2=50:50	520	48,1	4,8	590
7	ANP:SiO_2=10:90	600	43,9	4,9	610

** calculation of sample mass increase (Δm) was carried out at conversion into ANP content in sample*

Testing the copper nanopowders showed that their oxidation started even at ~180 °C (table 4, samp. 1), while the oxidation of coarsely dispersed powders of the given metal started at 240 °C. Small size of particles is also responsible for high velocity of oxidation achieved 1,7 mass. % per minute, the degree of powder oxidation amounting 15,5 mass. %.

It was stated that the presence of inorganic oxides increased temperature of CNP oxidation start insufficiently: from 180 to 190 °C. But mass content of oxides in samples did not affect this value.

Addition of small quantity of such chemically inert oxide as Al_2O_3 to the mixture resulted in increasing the degree of CNP transformation (table 4, samp. 1, 2). Further increasing the content of the additive in the samples (table 4, samp. 3, 4) resulted in decreasing the degree of CNP transformation at heating. Similar dependence was observed at addition of SiO_2 into the mixture (table 4, samp. 1, 5–7).

Table 4. *Parameters of copper nanopowders oxidation in mixtures with aluminium, silicon and manganese (II) oxides*

№	Content	Temperature of oxidation start T_0 (±5), °C	Degree of sample oxidation, Δm* (±2 %), mass. %	Maximum oxidation velocity, V_{ox}, mass %/min	Temperature of finishing intensive oxidation, T_{io}, °C
1	ANP	180	15,5	1,7	220
2	ANP:Al_2O_3=90:10	190	17,0	1,5	210
3	ANP:Al_2O_3=50:50	190	12,4	1,4	220
4	ANP:Al_2O_3=10:90	190	9,8	0,7	–
5	ANP:SiO_2=90:10	190	16,7	1,7	210
6	ANP:SiO_2=50:50	190	9,2	1,4	220
7	ANP:SiO_2=10:90	190	7,1	0,9	350

** calculation of sample mass increase (Δm) was carried out at conversion into CNP content in sample*

Maximum velocity of sample oxidation with additives decreased in comparison with CNP without additives. Raising the content of both Al_2O_3 and SiO_2 in the mixture the velocity of oxidation processes in the nanopowders slowed down.

Conclusion

1. The analysis of activity parameters showed that addition of Al_2O_3, SiO_2 and MnO_2 in the powder form into aluminium nanopowders increased the stability of nanopowders to oxidation: the temperature of oxidation start raised, the degree of sample oxidation decreased in comparison with the initial samples. At the same time oxide additives into copper nanopowder first resulted in increase (by 10 °C) of the temperature and then did not affect the temperature of oxidation start, that remained practically constant and amounted 190 °C.
2. When diluting aluminium nanopowders by aluminium and silicon oxides the temperature of oxidation start increased by 90 and by 100 °C correspondingly. The maximum velocity of aluminium oxidation after addition of 10 % Al_2O_3 1,25 decreased 1,25 less, but at further diluting it constantly raised: adding 90 % Al_2O_3 it did 1,8 times more. Perhaps, after partial oxidation of aluminium nanopowder and reaching the temperature of SiO_2 melting, the process of oxidation-reduction notably slowed down, that was in the first place apparent in decrease of aluminium oxidation degree from 50,3 to 43,9 of mass. %.
3. For copper the heating effect at its oxidation is sufficiently lower. In contrast to aluminium nanopowder mixture the temperature of copper oxidation start did not change and amounted 190 °C for mixtures with Al_2O_3 and SiO_2. Small addition of oxides (10 mass. %) increased the degree of nanopowder oxidation, but when increasing the content of oxides the oxidation degree decreased. The addition of oxides slowed down the maximum velocity of oxidation: from 1,7 to 0,7 mass. % per minute adding Al_2O_3 and from 1,7 to 0,9 mass. % per minute in the case with SiO_2, that can be explained by decreasing heat conductivity of mixtures. The constancy of the temperature of oxidation start proves the results on the structure of double electric layer obtained before preventing copper from oxidation. Destruction of that layer (electric disruption) takes place at a strictly definite temperature 190 °C, or at 160...170 °C for the samples obtained in different conditions.

Literature

1. Nazarenko O.B. Electroexplosive nanopowders: production, properties, application. – Tomsk: TSU press, 2005. – 148 p.
2. Khabas T.A., Vereshchagin V.I. Synthesis of complex compounds in bipair and triple oxide systems with the additives of nanodispersed aluminium // New castables. – 2003. – № 36. – P. 35–38.
3. Teipel U. Energetic Materials. – Heppenheim: Litges and Dopf Buchbinderei GmbH, 2005. – P. 237–292.
4. Ilyin A.P., Gromov A.A. Burning of aluminium and boron in the ultrafine state. – Tomsk: TSU press, 2002. – 154 p.
5. Quartzkhava I.F., Plutto A.A., Chernov A.A., Bondarenko V.V. Electric explosion of metallic wires // The Journal of theoretical physics. – 1956. – V. 30. – № 1. – P. 42–53.
6. Tikhonov D.V. Electroexplosive production of ultradispersed powders of complex composition: Dissert. ... cand. of tech. science. – Tomsk, 2000. – 237 p.
7. Bulanov V.Ya., Quater L.I. Diagnostics of metallic powders. – Moscow: Nauka, 1983. – 278 p.
8. Ilyin A.P., Gromov A.A., Yablunovsliy G.V. On the activity of aluminium powders // Физика горения и взрыва. – 2001. – Т. 37. – № 4. – С. 58-62.
9. Wendlandt W. Thermal methods of analysis / Trans. from English, edited by V.A. Stepanov, V.I. Bernstien. – Moscow, 1978. – 526 p.
10. Amelkovich Yu.A., Godymchul A.Yu. Ilyin A.P. Oxidation of copper and aluminium nanopowders in the mixture with inorganic oxides // Physicochemostry of ulradispersed (nano-) systems: Materials of the VII All-Russia conf. – Zvenigorod, 22–24, November 2005. – Moscow: MRPI, 2005. – P. 148–149.