Chemistry for Sustainable Development **22** (2014) 393–400

UDC 546.57:546.56:546.74:546.87:66.094.1

Preparation of Metal Nanopowders by Reduction in Organic Liquids

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Abstract

The products formed at the reduction of silver, copper, nickel and bismuth carboxylates were investigated by methods of chemical, X-ray phase, differential thermogravimetric analyses and electronic microscopy at heating in the environment of high-boiling organic liquid. It was shown that powders of silver, copper, nickel, bismuth and of alloys of these metals of the submicron size could be obtained by the way of reduction of these metals carboxylates by ethylene glycol and benzyl alcohol. Structural morphological features of powders obtained, as well as the influence on these parameters of the length of the methylene chain of the starting carboxylate, its morphology and the process of doping by cations of other metals were investigated.

Key words: nanopowders of silver, copper, nickel and bismuth, these metals carboxylates, ethylene glycol, benzyl alcohol, reduction

INTRODUCTION

The development of the preparation methods for various substances in the nanodisperse state is one of the most important goals of modern materials science. This is conditioned by the ability to create based on them materials and products of the new generation with outstanding consumer properties. Lately, nanomaterials based on silver, copper, nickel and bismuth nanoparticles serve as the object of intensive investigations, since their optical and physicochemical properties differ significantly from properties of materials based on massive particles [1, 2]. Due to this, they can be broadly used in electronics, chemical catalysis and medicine.

One of the preparation ways of metals of the submicronic size is the method of reduction of their organic or inorganic salts in the medium of a high-boiling organic liquid. Usually, in such processes, as the reductive environment, aliphatic polyols – glycerine, ethylene glycol, triethylene glycol and tetraethylene glycol, are used [3–6]. It is noteworthy that polyol itself (high molecular mass alcohol) acts not only as a reducing agent for the preparation of metals nanoparticles but also as a stabilizer limiting the particles growth and hindering their agglomeration. In addition to high molecular mass alcohols, benzyl alcohol (monatomic aromatic alcohol) with the boiling point of 205 °C having a high reduction potential can be used for these purposes. In our opinion, at the synthesis of metals nanoparticles as the starting compound, it is desirable to use carboxylic acid salts that are also stabilizers. Metal nanopowders obtained herewith should perfectly match with organic compounds of a various nature, what will open up the possibilities for the creation of qualitative polymeric composition materials.

The present work is devoted to the preparation of nanoparticles of silver, copper, nickel and bismuth, as well as alloys based on them by reduction of these metals carboxylates by ethylene glycol and benzyl alcohol.

EXPERIMENTAL

Silver, copper, nickel, bismuth nitrates and sodium hydroxide of the Kh. Ch. (chemically pure) reagent grade, butyric, caproic and caprylic acids of the Ch. (pure) reagent grade, stearic and formic acids, ethylene glycol and benzyl alcohol of the Ch. D. A. (pure for analysis) reagent grade, medical ethyl alcohol (95 %) were used in the work. Solutions were prepared using distilled water.

The synthesis of metal carboxylates was carried out by the way of an exchange reaction between sodium salt of the corresponding acid and an aqueous solution of silver, copper, nickel or bismuth nitrate according to the reaction

$$z(C_nH_{2n-1}O_2Na) + Me(NO_3)_z \rightarrow (C_nH_{2n-1}O_2)_zMe + zNaNO_3 \quad (1)$$

where $z = 1$ for silver, $z = 2$ for copper and nickel, $z = 3$ for bismuth.

Reduction of powders of metals carboxylates was implemented at the process temperature of 100–205 °C depending on the nature of the reducible metal under reduction and solvent at the mass ratio liquid/solid, equal to (3–10) : 1. The mixture was heated with stirring up to a pre-selected temperature and kept under these conditions till the reduction process completion. The resulting powder was separated from the solvent, washed with ethyl alcohol and air dried. The time required for the complete reduction of the specific compound was determined experimentally based on X-ray phase and chemical analyses of the resulting products. Research objects in the work were silver, nickel, copper and bismuth carboxylates (formiates, caprylates and stearates).

X-ray phase analysis (XPA) of deposition products was carried out using a Bruker D8 Advance diffractometer (CuK_α radiation, the rate of rotation of counter is 0.1 °/min). The samples study by the method of transmission electron microscopy (TEM) was carried out using a JEM-2010 and JEM-2000 FXII electronic microscopes (JEOL, Japan) with 200 kV accelerating voltage. The samples study by the method of raster electron microscopy (REM) was carried out using a Hitachi TM 1000 and Hitachi 3400 N scanning electronic microscopes (Hitachi Ltd., Japan).

The content of silver, copper, nickel and bismuth in solutions and solid products was determined by the atomic absorption method on a Spectra AA 280 FS spectrophotometer (Varian, Australia) or by potentiometric titration depending on quantities. Solid products before the determination were preliminary treated with a solution of nitric acid with the concentration of 6 mol/L.

RESULTS AND DISCUSSION

Reduction of silver compounds

It was established that silver butyrate, caproate the caprylate and stearate represented themselves needle-like crystals of the length of 5–30, 3–15, 1–5 and 0.5–2 μm, respectively. At dissolution of silver caprylate in caprylic acid and organic solvents, the concentration of silver in solutions obtained at (23±2) and (100±2) °C is, correspondingly (g/L): 0.04 and 0.30 (caprylic acid); 1.31 and 4.00 (benzyl alcohol); 0.16 and 0.58 (ethylene glycol); 0.08 and 0.34 (glycerine); 0.008 and 0.018 (octyl alcohol); 0.011 and 0.016 (octane); 0.007 and 0.007 (toluene). Herewith, in case of ethylene glycol, octyl alcohol and glycerine at heating the solution up to 100 °C a partial reduction of silver takes place.

According to roentgenographic data, the size of silver particles obtained by the thermal decomposition in air of silver butyrate, capronate, caprylate and stearate is of the order of 40–80 nm, but they are bound in durable agglomerates of the size of 10–60 μm, not dispersible in organic solvents. For the purpose of obtaining silver nanoparticles as individual particles, the variant of reduction of silver carboxylates in ethylene glycol was considered. According to data of TEM of powders of silver metal obtained as a result of reduction of silver butyrate, capronate, caprylate and stearate by ethylene glycol, the particles shape is close to spherical. The conducted calculation of the particles distribution by sizes shows that in case of reduction of silver butyrate the diameter of the basic massif of silver nanoparticles varies in the limits of 25–100 nm with the average size of 73 nm (Fig 1, *a*); in case of caproate – 20–80 nm at the average size of 48 nm, caprylate – 10–50 nm with the average size of 32 nm and stearate – 5–30 nm, with the average size of

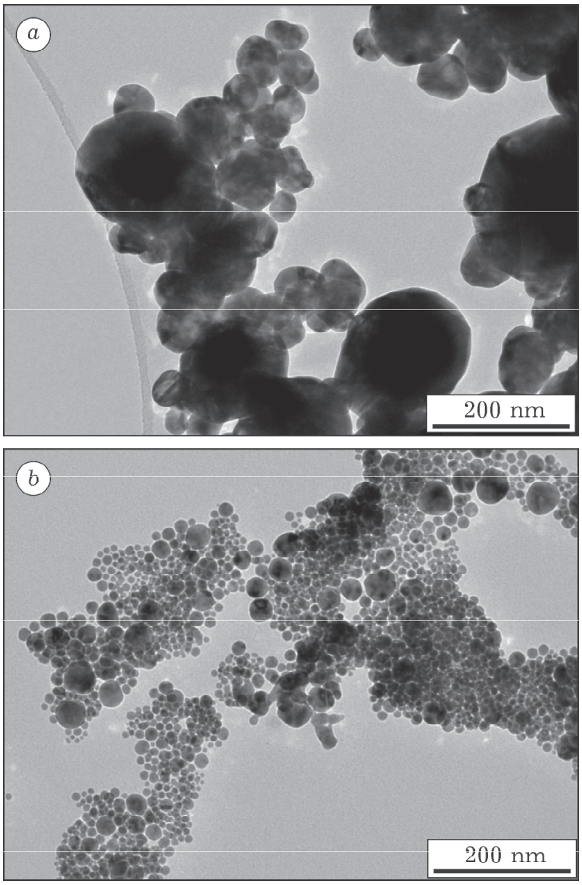

Fig. 1. Electron micrographs of powders of silver metal obtained as a result of reduction of silver butyrate (*a*) and stearate (*b*) in ethyleneglycol.

16 nm (see Fig. 1, *b*). According to XPA data, silver obtained by reduction of its compounds by ethylene glycol or benzyl alcohol is present in the metal kind: peaks corresponding to the oxide phase were not detected.

The analysis by the method of X-ray photoelectron spectroscopy of samples of silver obtained by reduction of silver caprylate by ethylene glycol also indicates that silver on the surface of the studied samples is exclusively in the metallic state, and silver particles are covered by an organic film. As follows from thermal analysis data, the content of organic impurities in silver particles does not exceed 1 % and they can be removed by heating at the temperature of the order of 250 °C.

From data of [7, 8] it follows that reduction of silver ions in case of ethylene glycol is mainly conditioned by the presence of glycolaldehyde forming as a result of oxidation of ethylene glycol by air oxygen at its heating according to the following scheme:

$$2HOCH_2CH_2OH + O_2 \rightarrow 2HOCH_2CHO + 2H_2O \quad (2)$$

Then, the reaction of reduction of silver, for example, caprylate can be represented apparently as

$$HOCH_2CHO + 2CH_3(CH_2)_6COOAg + H_2O \rightarrow 2Ag + HOCH_2COOH + 2CH_3(CH_2)_6COOH \quad (3)$$

The formation of caprylic acid at reduction of silver caprylate by ethylene glycol is supported by the fact that as a result of the addition to the organic phase of aqueous solutions of silver or bismuth compounds, these metals caprylates are precipitated, which is evidenced by data of XPA of compounds obtained. Therefore, caprylic acid forming in the course of reduction can be used for the synthesis of starting materials.

It should also be noted that silver nanoparticles obtained at reduction of silver caprylate are dispersed well in organic solvents. Due to this; they can be used for creating stable colloidal systems based on silver with various areas of applications, for example, for the production of electroconductive inks, glues and pastes based on organic solvents or binders.

Reduction of nickel compounds

The studies conducted on reduction of nickel formiate of the composition $Ni(HCOO)_2 \cdot 2H_2O$ in the medium of benzyl alcohol show that in proportion to heating the suspension in the range of temperatures of 150–170 °C salt dehydration occurs. The formation of nickel noticeable on a darkening of the suspension starts after several minutes after reaching the boiling temperature (205 °C). A full conversion of nickel formiate into the metal happens approximately in 3 h after start of boiling. Nickel is formed in the form of a voluminal, weakly aggregated powder, the content of impurities in which (including oxygen) does not exceed 0.2 %. However, it is unclear to what extent the formation of nickel is associated with reduction of formiate by benzyl alcohol. The fact is that nickel formiate is thermally unstable and at heating in the inert gas atmosphere or under vacuum it decomposes to form metallic nickel. Herewith, nickel is formed as very small (size of up to 1–2 nm) pyrophorous particles

[9–12]. The process is of the topochemically character and proceeds through the formation and growth of the nuclei of the metal phase in the matrix of the starting crystals [11].

From the thermogram of the decomposition of nickel formiate under isothermal conditions in the helium atmosphere, it follows that heating during 3 h at the temperature of 180 °C leads only to the removal of crystallization water, and the noticeable decomposition of formiate does not occur. However, at 200 °C formiate decomposes completely up to metallic nickel after 130 min after the start of heating. Although the decomposition of formiate under the liquid layer goes considerably slower than in the gas atmosphere [9], one can suggest that at boiling in benzyl alcohol two processes occurring in parallel are implemented. In one of them (thermal decomposition), the reducing agent of nickel ion is the anion of formic acid and in the other one – molecules of benzyl alcohol. Benzyl alcohol, herewith, is oxidized to benzaldehyde that has the boiling point of 176 °C and is evaporated, as the formation. The condensate obtained by passing vapours through a condenser that is allocated from the reaction vessel was analyzed by the method of liquid chromatography. Judging by the content of benzaldehyde in it, at least, 45 % of nickel is formed as a result of reduction of formiate by benzyl alcohol. As a result of the conducted research, the preparation method of submicron nickel powder by the thermal decomposition of nickel formiate in the medium of benzyl alcohol at the temperature of 195–205 °C [13] was developed.

It should be noted that the participation of benzyl alcohol in the process of reduction of nickel formiate has a strong influence, in the first place, on dimensional features of the resulting powder. The average diameter of particles increases tenfold, in comparison with the thermal decomposition in the inert gas atmosphere and reaches 500 nm (Fig. 2, *a*). But, in general, the reduction process in benzyl alcohol keeps features, characteristic for the thermal decomposition of a dry salt: the presence of the induction period, formation and growth of embryos of the metal phase (see Fig. 2, *b*).

This circumstance opens up the principal possibility of the impact on the final size of nickel particles by the rate change of the formation and growth of embryos. The method, known in solid state chemistry, based on doping of nickel formiate by cations of other metals was used for the implementation of this idea. Cations of silver, copper and bismuth were investigated as such dopants. The introduction of doping cations into the crystalline lattice of nickel formiate was carried out by the method of the co-precipitation of a mixture of nickel nitrates and the corresponding metal by sodium formiate.

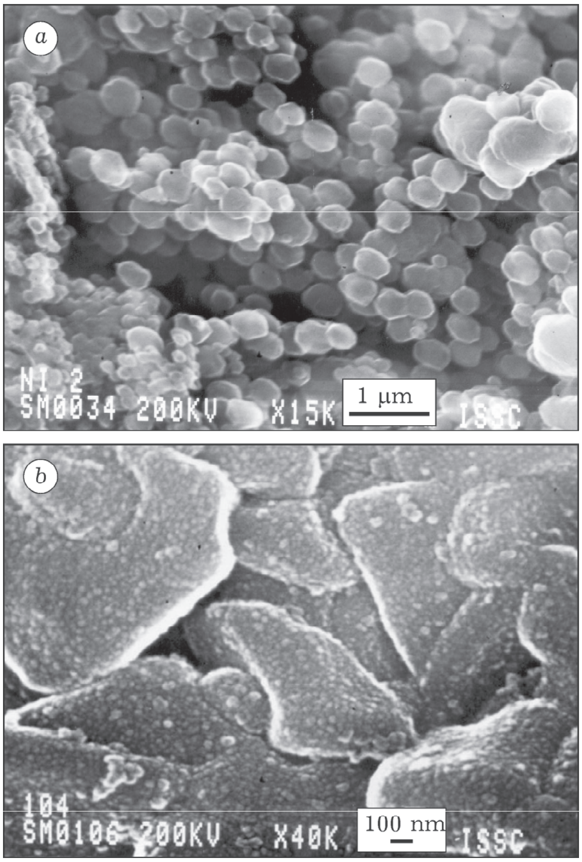

Fig. 2. Electronic micrographs of nickel particles obtained by reduction of nickel formiate in benzyl alcohol (*a*) and at the starting stage of reduction (*b*).

The process of reduction in benzyl alcohol proved to be sensitive to the introduction of silver ions in the lattice of nickel formiate. Herewith, the duration of the inductive period is decreased and the time of a complete reduction of nickel is shortened in more than three times. However, an important effect consists in that a more fine powder of nickel is obtained as a result of doping by silver ions. When introducing 0.1 mol. % of silver the average size decreases to 50 nm. Doping nickel formiate by copper ions in the same concentration influences the reduction rate insignificantly; however, the size and shape of particles are changed significantly. Particles become plane and have the shape of hexagonal plates of the size of from 100 up to 500 nm. Doping by bismuth does not influence on the shape of particles, they remain predominantly spherical, but their average size is markedly decreased and amounts to 100–200 nm.

Unlike nickel formiate, insoluble in benzyl alcohol, and interacting with it in the solid state, nickel caprylate and stearate are almost completely dissolved when heated and the mass ratio salt/benzyl alcohol, equal to 1 : 5 and higher. Thus, when dissolving nickel caprylate in caprylic acid and organic solvents at the temperature (23±2) °C the concentration of nickel in the resulting solutions amounts to (g/L): 61.3 (caprylic acid), 53.5 (toluene), 15.6 (benzyl alcohol), 14.8 (octane), 1.36 (ethylene glycol), 1.32 (ethyl alcohol). At the temperature of 205 °C, nickel caprylate and stearate are thermally stable; therefore, nickel is formed only as a result of their reduction by benzyl alcohol. Reduction starts simultaneously with the start of boiling of the solution and already after 7 to 10 min a voluminous precipitate containing nickel (as the powder form) and large agglomerates (in the form of a thin foil) with the size of up to several millimetres are formed. Reduction ends approximately in 1 h after the start of boiling. With the change of the length of the carbon chain, at the transition from formiate to stearate, the average size and morphology of nickel particles are changed. In case of caprylate, these are predominantly spherical particles of the size of about 200 nm and when reducing stearate needle particles of the thickness of 100–150 nm and length up to 500–600 nm and plates of the size up to 500 nm are formed.

It should be noted that submicron powders of nickel obtained as are result of reduction of carboxylates can be used in the electronic industry for the production of multilayer capacitors and manufacture of filter elements.

Reduction of copper compounds

When reducing copper formiate of the composition of $Cu(HCOO)_2$ in benzyl alcohol at the temperature of 190 °C for 10 min copper formiate is reduced to copper (I) oxide Cu_2O, the further reduction of which to the metal proceeds very slowly. The increase of the temperature up to 200 °C and dwell time up to 3 h proved to be insufficient to achieve full reduction. Therefore, in case of copper formiate a high reduction potential of benzyl alcohol leads to the negative effect changing the process direction. So, instead of the reaction of the thermal decomposition leading to the preparation of metal copper, the reduction reaction to form copper (I) oxide is implemented.

A quite different behaviour is demonstrated by copper caprylate, which is well dissolved in organic solvents. Thus, when dissolving copper caprylate in caprylic acid and organic solvents at the temperature of (80±2) the concentration of copper in the resulting solutions amounts to (g/L): 42.2 (caprylic acid), 68.0 (toluene), 26.5 (benzyl alcohol), 18.6 (octane), 10.5 (60 °C) (ethyl alcohol), 1.1 (ethylene glycol), 0.95 (glycerine). Copper caprylate is thermally more stable, than formiate; therefore, the dominating process here, apparently, is reduction by molecules of the liquid. In benzyl alcohol at the boiling point (205 °C), caprylate is also converted pretty quickly into copper (I) oxide Cu_2O and then slowly, during 3 h, reduced to metal copper. Cu_2O particles have the shape, close to spherical and size of from 100 to 200 nm (Fig. 3, *a*). A part of copper particles formed at their further reduction preserve the same shape and sizes, but herewith, a significant amount of larger particles and particles with a completely different acicular shape are contained in the product (see Fig 3, *b*). Apparently, reduction of Cu_2O particles in this case proceeds through their dissolution and subsequent precipitation in the form of metal copper. The addition to benzyl alcohol of silver caprylate in the amount of 0.1 mol. % in relation to copper caprylate does not affect the size and shape of Cu_2O particles. Herewith, the size and shape of copper particles, derivable herewith, coincide with the size and shape of Cu_2O particles. Accordingly, in the presence of silver the process of reduction of Cu_2O particles can go into the solid-phase mode.

When reducing copper carboxylates by ethylene glycol with the increase of the temperature up to 190 °C the process pass through the stage of the formation of copper glycolate of

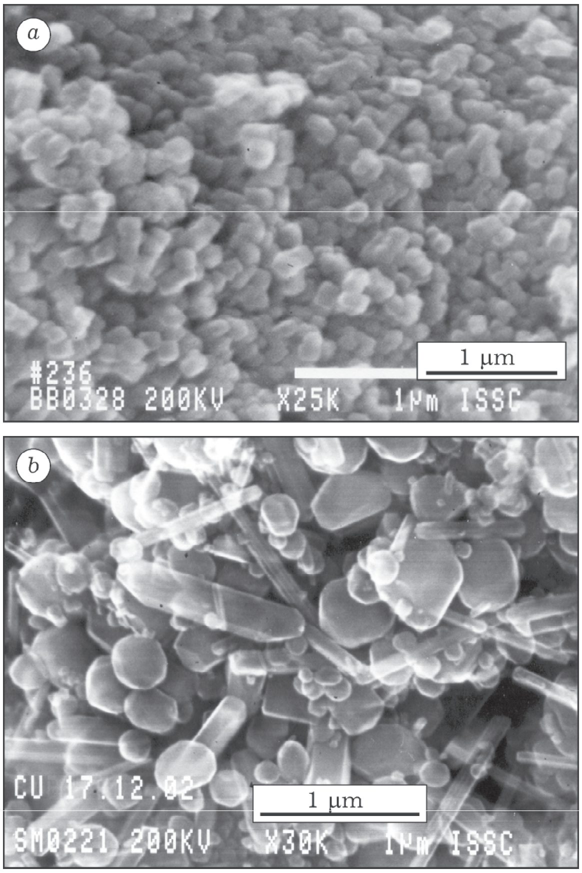

Fig. 3. Electronic micrographs of reduction products of copper caprylate with benzyl alcohol: *a* – particles of copper (I) oxide, *b* – copper particles.

the composition $Cu(CH_2OCH_2OH)_2$ followed by its reduction to the metal. The copper particles formed herewith have the size of ~200 nm. When adding copper carboxylates in ethylene glycol, preheated up to 180 °C and when stirring the mixture for 30 min the size of the formed particles of copper metal is equal to 130, 70 and 38 nm in case of 2-ethyl hexanoate, caprylate and stearate, respectively.

Reduction of bismuth compounds

As a result of the process study of forming finely crystalline powders of bismuth metal obtained at the thermal (150–205 °C) decomposition of its compounds of various nature in benzyl alcohol, it was established that the efficiency of bismuth reduction up to the metal increased in the row: oxochloride < oxonitrate < oxocarbonate < oxide < oxogallate < bismuth bitartrate. Herewith, the final stage of the thermal decomposition of bismuth metal of the spherical shape with the size of 0.1–1 µm.

At the thermal decomposition of bismuth oxide by benzyl alcohol at 205 °C for 7 h, particles of the spherical shape with the size of 0.1–0.5 µm are also formed, while in case of its decomposition in the medium of ethylene glycol at 190 °C during 4 h, metal particles of the hexagonal shape of the size of the order of 0.5 µm and thickness of 0.01–0.03 µm (Fig. 4, *a*) are formed. When interaction bismuth oxide with benzyl alcohol as a result of passing vapours through a condenser released in the course of the reaction, the condensate was obtained. Its analysis by the method of liquid chromatography showed that the reaction of reduction proceeded with the formation of benzaldehyde and could be represented as

$$\mathrm{Bi_2O_3\,(solid)} + \mathrm{3C_6H_5CH_2OH\,(solution)} \rightarrow \mathrm{2Bi\,(soild)} + \mathrm{3C_6H_5CHO\,(solution)} + \mathrm{3H_2O} \quad (4)$$

The conducted studies of the thermal decomposition of bismuth monocarboxylates with a various length of the methylene chain by benzyl alcohol showed that the product of the decomposition of bismuth formiate, oxocaprylate and oxostearate was powdery bismuth metal of the spherical shape with the size of particles of 0.1–1 µm. Electronic micrographs of particles of bismuth metal obtained as a result of reduction of bismuth stearate in benzyl alcohol are shown in Fig. 4, *b*. It should be noted that at reduction of bismuth carboxylates by ethylene glycol with the increase of temperature up to 190 °C the process occurs through the stage of the formation of bismuth glycolate of the composition of $Bi(C_2H_4O_2)_3$ and its subsequent reduction to the metal. The bismuth particles formed herewith have the size of 80–120 nm. When adding bismuth carboxylates in to ethylene glycol preheated up to 180 °C and stirring the mixture for 30 min, the size of the formed particles of bismuth metal amounts to 80, 72 and 58 nm in case of bismuth oxoformiate, oxocaprylate and oxostearate, respectively.

The method of the preparation of powdered bismuth with the size of particles of 0.03–3 µm by reduction of bismuth monocarboxylates in the presence of benzyl alcohol or ethylene glycol [14] was developed in the course of the conducted studies.

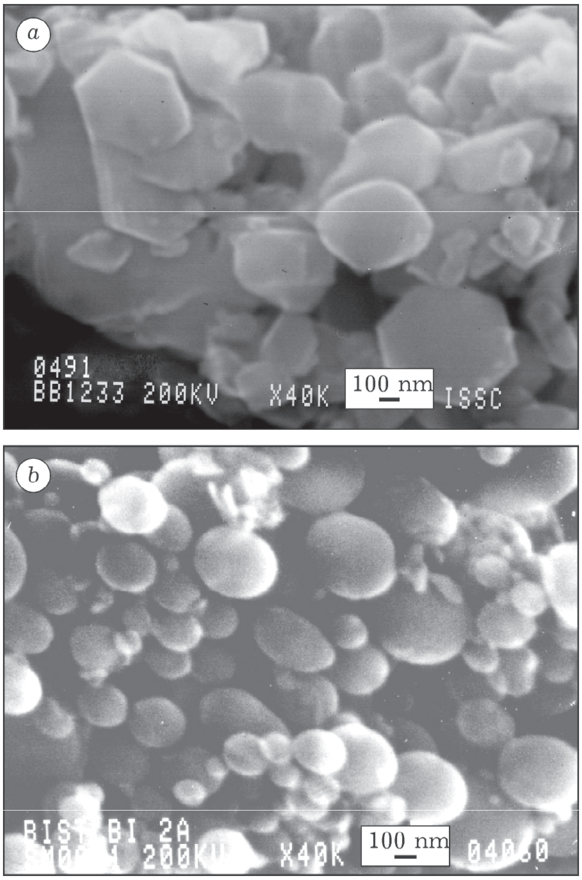

Fig. 4. Electron micrographs of the products of reduction of bismuth oxide in the medium of ethylene glycol at 190 °C for 4 h (*a*) and bismuth stearate by benzyl alcohol (*b*).

Preparation of silver alloys with copper or bismuth, of bismuth with copper

Alloys of silver with copper or bismuth, as well as those of bismuth with copper are of interest for the practical application. The research conducted earlier showed [15] that reduction of a mixture of silver and bismuth stearates is promising for the preparation of alloys of these metals of the submicron size. As the starting mixture of metal carboxylates both their mechanical mixture and the compounds obtained as a result of the reaction of the cationic exchange can be used. Thus, in the system solid silver carboxylate – a solution of bismuth or copper nitrate, the exchange reaction in case of caprylic acid occurs according to the equation

$$n(C_7H_{15}COOAg)\ (\text{org.}) + Me^{n+}_{aq} = (C_7H_{15}COO)_nMe\ (\text{org.}) + nAg^{+}_{aq} \tag{5}$$

where $n = 3$ for Bi and $n = 2$ for copper.

Electronic micrographs of alloys of silver (70 %) and copper (30 %), as well as silver (80 %) and bismuth (20 %) obtained at reduction of a mixture of appropriate caprylates by ethylene glycol at 170 °C are given in Fig. 5.

It should be noted that copper nanopowders modified with silver can be obtained as a result of the treatment of powdery copper by a solution of silver nitrate in ethylene glycol in the presence of a carboxylic acid. Herewith, one can implement the effective electrochemical reduction of silver according to the reaction

$$Cu + 2AgNO_3 = Cu(NO_3)_2 + 2Ag \tag{6}$$

Copper ions formed in the course of the reduction reaction interact with carboxylic (caprylic) acid according to the reaction

$$Cu(NO_3)_2 + 2C_7H_{15}COOH = (C_7H_{15}COO)_2Cu + 2HNO_3 \tag{7}$$

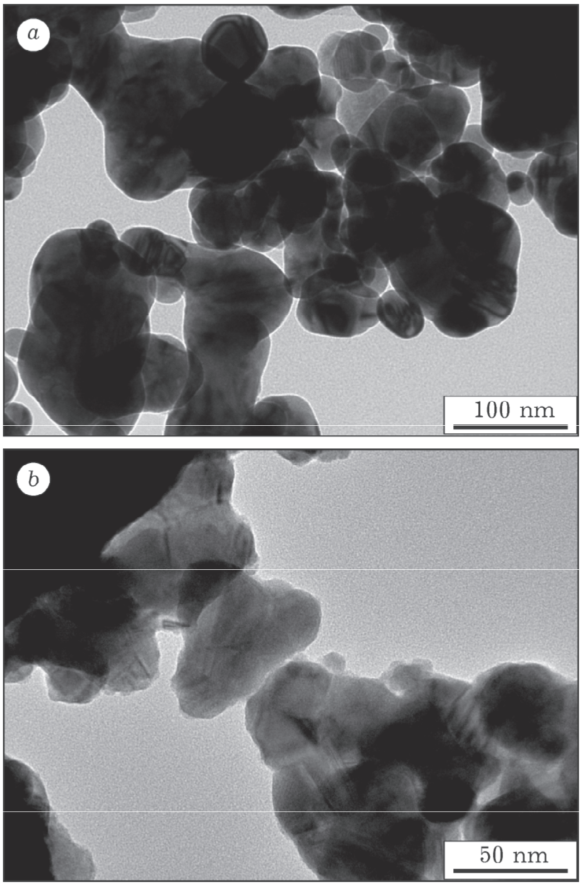

Fig. 5. Electron micrographs of alloys of silver with copper (*a*) and of silver with bismuth (*b*) obtained at reduction of a mixture of appropriate caprylates by ethylene glycol.

Herewith, copper carboxylate is formed as a result of the interaction, which hinders copper oxidation. It is advisable to use acids with the length of the methylene chain of C_4–C_{10} as a carboxylic acid. They interact effectively with copper ions forming carboxylates and at the ordinary temperature are liquids, what allows effectively separating the final products at the stage of rinsing with organic solvents.

CONCLUSION

The process of the thermal decomposition of nickel, copper, silver, and bismuth monocarboxylates in the medium of benzyl alcohol or ethylene glycol was studied. The possibility of the preparation of powders of these metals with the micron and submicron sizes was shown.

It was shown that reduction of a mixture of these metals monocarboxylates was promising for the preparation of alloys of metals of the submicron size.

The possibility of the preparation of powdery copper modified with silver as a result of the treatment of copper with a solution of silver nitrate in ethylene glycol in the presence of a carboxylic acid was shown.

REFERENCES

1 Gusev A. I., Rempel A. A., Nanokristallicheskiye Materialy, Fizmatgiz, Moscow, 2001.

2 Khelbtsov N. G., Dykman L. A., *J. Quant. Spectr. Radiat. Transfer*, 111, 1 (2010) 1.

3 US Pat. No. 4539041, 1985.

4 Fiévert F., Lačier J. P., and Fiмlarz M., *MRS Bull.*, 14, 12 (1989) 29.

5 Ducamp-Saněuesa C., Herrera-Urbina R., and Fiělarz M., *J. Solid State Chem.*, 100 (1992) 272.

6 Orel Z. C., Matijević E., and Goia D. V., *J. Mater. Res.*, 18, 4 (2003) 1017.

7 Skrabalak S. E., Wiley B. J., Kim M., Formo E. V., Xia Y., *Nano Lett.*, 8 (2008) 2077.

8 Panfilova E. V., Khlebtsov B. N., Burov A. M., Khlebtsov N. G., *Kolloid. Zh.*, 74, 1 (2012) 104.

9 Balandin A. A., Grigoryan E. S., Yanysheva Z. S., *Zh. Obshch. Khim.*, 10, 11 (1940) 1031.

10 Bircumshaw L. L., Edwards J., *J. Chem. Soc.*, (1950) 1800.

11 Brown M. E., Delmon B., Galwey A. K., McGinn M. J., *J. Chim. Phys.*, 75 (1978) 147.

12 Edwards A. B., Garner C. D., Roberts K. J., *J. Phys. Chem. (B).*,101, 1 (1997) 20.

13 RU Pat. No. 2233770, 2004.

14 Lazarini F., *Acta Crystallogr.*, 34, 11 (1978) 3169.

15 Mikhailov Yu. I., Yukhin Yu. M., Shcherbinina V. N., Logvinenko V. A., *Zh. Neorg. Khim.*, 36, 8 (1991) 1913.

16 RU No. 2225282, 2002.

17 Bokhonov B. B., Yukhin Yu. M., *Zh. Neorg Khim.,* 52, 6 (2007) 993.