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PHYSICAL METHODS OF INVESTIGATION

Morphologic Characteristics of Bismuth and Silver Particles Formed upon the Reduction of Metal Stearates with Benzyl Alcohol

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Abstract—The products of the reduction of individual and mixed bismuth oxohydroxostearate and silver stearate with benzyl alcohol are studied by electron microscopy and X-ray powder diffraction. The reduction of mixed bismuth and silver carboxylates with benzyl alcohol is a promising route to both individual submicronzised bismuth and silver metal powders and to their alloys.

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Metallic bismuth has several unique properties which make it attractive for practical applications. Bismuth is used in nuclear engineering for manufacturing polonium, and its alloys are used as high-temperature heat-transfer agents. Alloys of bismuth are used extensively: tellurium alloy is used in refrigerators and thermogenerators; antimony and tellurium alloys are used as thermoelectric cells in solar thermoelectric generators; chromium, indium, europium or manganese alloys, as magnetic materials; silver and cesium alloys, as photocathodes in photomultipliers; silver and sulfur alloys, in semiconductor devices; and silver and tin alloys, as solders [1]. It is believed that bismuth, which has semimetal properties, acquires semiconductor properties in response to decreasing crystallite size. The magnetoresistance effect observed in single crystals and thin films also expands the applications of bismuth. For example, the range of electrons at room temperature is 100 to 600 nm [2]. These facts have stimulated researchers to search for new methods and to modify the existing methods for manufacturing nanometer- and submicron-sized bismuth.

Bismuth nanoparticles with sizes of 15 to 35 nm were prepared by the reduction of microemulsions of organobismuth compounds with dioctyl ether (a high-boiling apolar solvent) [3]. Metallic bismuth was obtained by the reduction of monoclinic bismuth oxide with supercritical isopropanol [4]. Bismuth nano- and microparticles were prepared by the reduction of bismuth salts with a polyatomic alcohol [5]. Nanocrystalline bismuth can also be prepared by the dispersion of metallic bismuth in paraffin at 280°C [6]. We demonstrated that powdered bismuth can be prepared via the reduction of its monocarboxylate to metal (by calcining at 200–250°C) under an inert atmosphere or in the presence of a high-boiling organic solvent [7].

Nanocrystalline silver also has interesting properties. Unlike for bismuth, the preparation of colloidal silver particles is well developed [8].

The formation of intermetallic compounds or bismuth-base alloys upon the reduction of mixtures of various metal salts is of the same interest as the manufacturing of metallic bismuth. The silver alloy of bismuth prepared by electrochemical deposition from alkaline solutions [9] is significant for application. Silver and bismuth metal powders are widely used in medicine [10, 11].

The phase diagram of the bismuth–silver system is a simple eutectic with limited solid solution regions [12]. The eutectic is formed at (265.5 ± 2)°C and contains 95.3 at. % bismuth. The solubility of silver in bismuth is infinitesimal; the solubility of bismuth in silver is 2.615 at. % at 500°C and 0.83 at. % at the eutectic temperature.

From mineral acid solutions, bismuth precipitates in the form of oxohydroxostearate $Bi_6O_4(OH)_4St_6$, where St is the stearate anion [13]. Associated metals are efficiently removed in this way. In turn, silver precipitates in the form of stearate AgSt from these solutions. EXAFS showed that silver stearate molecules form dimers $Ag(OOC_nH_{2n-1})_2$ with longer Ag–O bonds, forming four-membered rings [14].

Here, we report the results of our investigation of the morphology of metal particles produced by the reduction of individual and mixed bismuth oxohydroxostearate (BiOSt) and silver stearate (AgSt) with benzyl alcohol solution.

The choice of benzyl alcohol was dictated by the following reasons. First, alcohols are widely used for the reduction of metals from their salts. Second, the boiling temperature of benzyl alcohol (205°C) is higher than the temperatures at which bismuth oxohydroxostearate and silver stearate are stable. This also should favor the decomposition of the test compounds. In addition, benzyl alcohol keeps newly formed metal particles from oxidation and agglomeration.

EXPERIMENTAL

Synthesis of bismuth(III) oxohydroxostearate. To distilled water (1.2 L) heated to ~80°C, stearic acid (61.0 g) and a solution of NaOH (8.0 g) in water (0.150 L) were added under stirring. To the resulting mixture, an aqueous solution (0.137 L) of bismuth perchlorate containing 333 g/L bismuth was poured gradually under stirring. The synthesis was performed in Teflon vessels equipped with stirrers. The mixture was stirred for 30 min. After 30 min of settling, the precipitate was filtered off in vacuum, washed on a filter with distilled water, and dried in air. The stock solutions of bismuth perchlorate (1000 g/L bismuth) were prepared by dissolving high purity grade bismuth oxide (os. ch. 13–3, Russia) in 7.0 M perchloric acid. Solutions with lower bismuth concentrations were prepared by diluting the stock solution with distilled water.

Synthesis of silver stearate. To distilled water (1.0 L) heated to ~80°C, added were stearic acid (48.5 g), a solution of NaOH (7.1 g) in distilled water (120 mL), 1.3 M HNO_3 (10 mL), and (in increments) a solution of silver nitrate (29.6 g) in water (120 mL). The mixture was stirred for 30 min. After 30 min of settling, the precipitate was filtered off, washed with water, and dried in air. When required, the products were washed with ethanol and dried in air in order to free bismuth oxohydroxostearate and silver stearate from unreacted stearic acid.

Both the synthesized individual AgSt and BiOSt and their mechanical mixtures in various proportions were reduced with benzyl alcohol. In addition, AgSt + BiOSt compositions were prepared by exposure of silver stearate crystals to bismuth perchlorate solution.

Bismuth nitrate solutions can also be used in the synthesis of bismuth oxohydroxostearate and its mixtures with silver, but care should be taken to avoid the contamination of the products with bismuth oxohydroxonitrate, which results from hydrolysis. The reduction of bismuth oxohydroxostearate, silver stearate, and their mixtures was performed as follows: to benzyl alcohol (50 mg), the chosen compound (5 g) was added, and the mixture was heated on a sand bath at 150–205°C for 2 h. The resulting metal powders were washed with ethanol and dried in air. The X-ray powder diffraction analysis of the products was carried out on a DRON-3 diffractometer using CuK_α radiation with a counter speed of 0.5 deg/min and $I = 1000$. Differential scanning calorimetry (DSC) curves were recorded on a DIFSI-550 instrument at a heating rate of 10 K/min. Electron micrographs were recorded using a JEM-2000FXII transmission electron microscope with an accelerating voltage of 200 kV. Bismuth and silver in liquid and solid phases were determined using atomic absorption on a Saturn 2M spectrophotometer. Before the determination, the synthesis products were treated with nitric acid (1 : 1) for 30 min.

RESULTS AND DISCUSSION

In the X-ray diffraction patterns of the solid products produced upon exposure of silver stearate crystals to bismuth perchlorate solution (Fig. 1), there are virtually no substantial changes in the positions of basal reflections while the bismuth concentration in the products is not higher than 10 at. %; extra basal reflections appear only when the bismuth ion concentration in the mixture reaches 20 at. %.

Silver stearate undergoes several phase transitions upon heating [15]. At 122°C, AgSt transforms to a high-temperature phase; at 147°C, the transition to the liquid-crystal state occurs. The DSC curves of the products obtained by the treatment of AgSt crystals by bismuth perchlorate solution (Fig. 2) show that the phase-transition temperatures increase with increasing bismuth concentration in the batch to 10%. Until 10 at. %, reflections from individual bismuth oxohydroxostearate do not appear in the X-ray diffraction patterns of AgSt crystals exposed to bismuth perchlorate solution and thermal features intrinsic to BiOSt are absent from the DTA curves. Therefore, we can suggest that mixed silver stearate and bismuth oxohydroxostearate are formed at these stages.

The morphologic investigation of silver stearate crystals exposed to bismuth perchlorate solution shows that AgSt crystals retain their habit even after the AgSt + 10 mol % BiOSt composition is formed. In the AgSt + 20 mol % BiOSt composition, a bismuth oxohydroxostearate phase is observed as individual particles both on the lateral faces and at the basal surface of AgSt crystals (Fig. 3a). This character of exchange reactions, with the product phase mainly formed on the lateral faces of the crystal, is due to the anisotropic layered structure of metal carboxylates.

Our investigation shows that the particle morphology resulting from the collective reduction of bismuth oxohydroxostearate and silver stearate with benzyl alcohol differs substantially from the particle morphol-

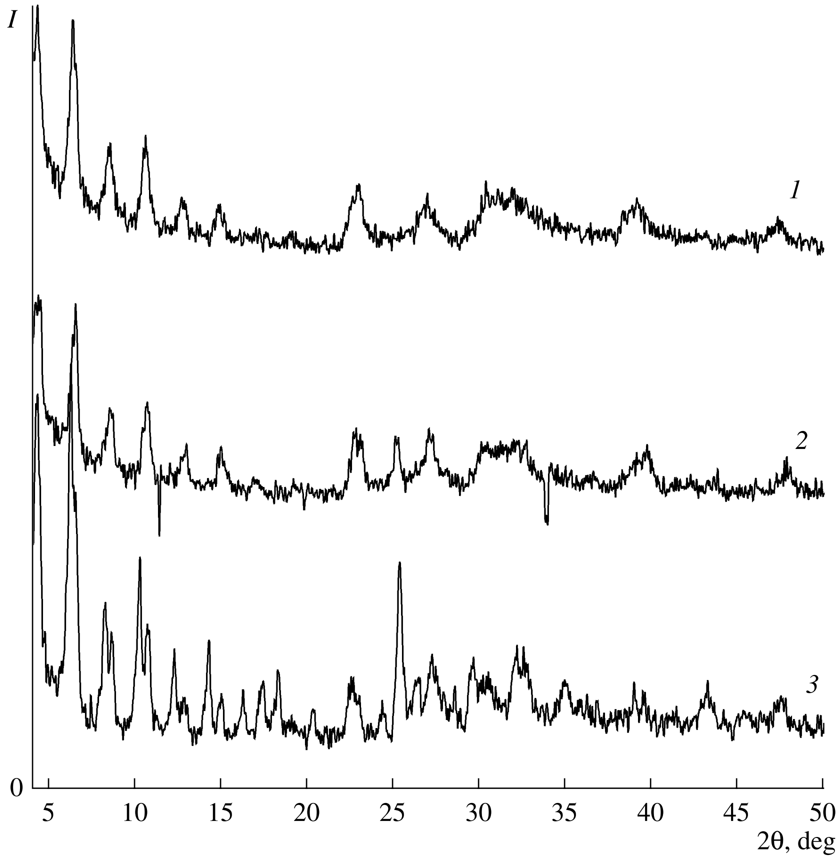

Fig. 1. X-ray powder diffraction patterns for (*1*) silver stearate and (*2*, *3*) its mixtures with bismuth oxohydroxostearate. The bismuth concentration (at. %) is (*2*) 10 and (*3*) 20.

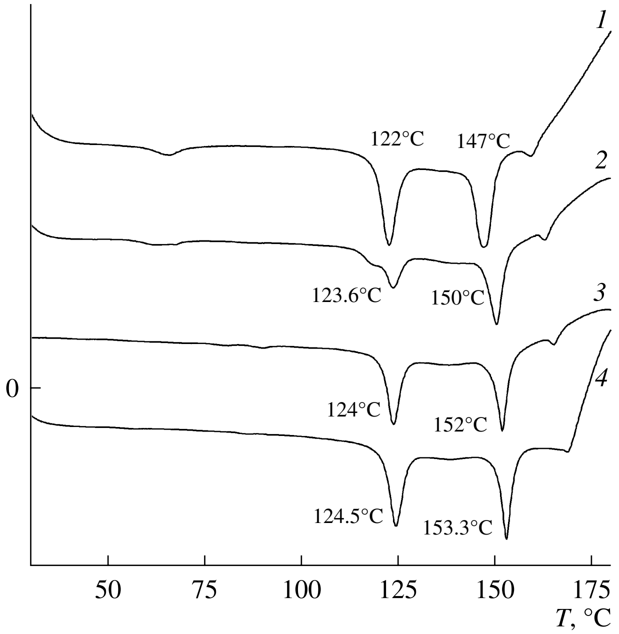

Fig. 2. DSC traces for (*1*) silver stearate and (*2–4*) its mixtures with bismuth oxohydroxostearate. The bismuth concentration (at. %) is (*2*) 2.5, (*3*) 5, and (*4*) 10.

ogy formed upon the reduction of the individual compounds.

The reduction of silver stearate with benzyl alcohol yields silver particles with sizes of 0.2 to 0.5 μm (Fig. 3b). Individual bismuth oxohydroxostearate yields spherical bismuth metal particles with sizes of 0.1 to 0.5 μm (Fig. 3c).

For the bismuth–silver alloy crystallizing upon the reduction with benzyl alcohol of a mechanical mixture of silver stearates and bismuth oxohydroxostearate or for the compositions obtained by the exchange reaction, the morphologic features differ significantly from the individual metal particles that are formed upon the reduction of metal carboxylates. In the AgSt + BiOSt composition obtained by the exchange reaction in which the bismuth oxohydroxostearate concentration is as low as 0.25 mol %, the reduction dramatically changes the morphology of the alloy: spherical aggregates with sizes up to 1 μm consisting of fine (~0.1 μm) silver and bismuth particles appear (Fig. 3d). Alloy particles with this morphology are formed upon the reduction of mixed bismuth oxohydroxostearate and silver

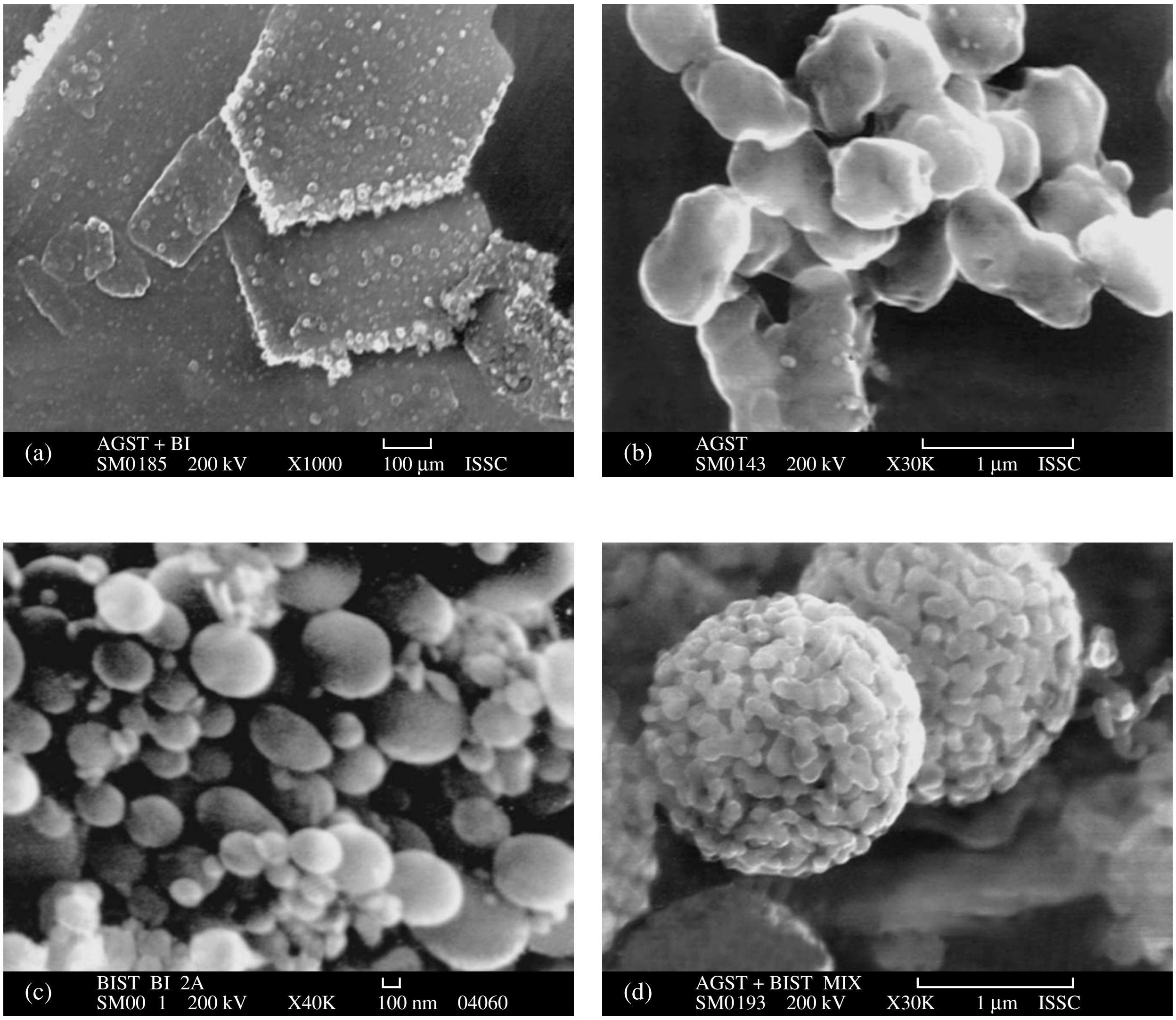

Fig. 3. Electron micrographs of (a) silver stearate single crystals containing 20 at. % bismuth, (b) silver metal particles, (c) bismuth metal particles, and (c) a mixture of the last two produced by the reduction of stearates in benzyl alcohol.

stearate over a wide concentration series, and they do not change until the bismuth oxohydroxostearate concentration reaches ~98 mol % in the AgSt + BiOSt mixture. When mechanical mixtures of AgSt and BiOSt powders are reduced with benzyl alcohol, alloy particles also crystallize in spherical aggregates of fine silver and bismuth particles. In our opinion, the morphologic similarity of the silver–bismuth alloy produced by the reduction of chemically synthesized mixed bismuth oxohydroxostearate and silver stearate and physical mixtures of these stearates, proves the liquid-phase character of the reduction. When bismuth oxohydroxostearate and silver stearate are treated with benzyl alcohol at 20°C, the bismuth and silver concentration in the alcohol is 0.82 and 0.05 g/L, respectively; with increasing temperature to 60°C, the bismuth concentration increases to 1.4 g/L.

It is notable that the amount of benzyl alcohol taken to reduce the metal stearates is substantially smaller than required by stoichiometry: the ligand with a long methylene chain also enhances the reduction of these compounds. This is proven the fact that the thermolysis of silver stearate and bismuth oxohydroxostearate in vacuum or air produces metallic silver and bismuth.

X-ray diffraction unambiguously confirms that silver and bismuth metal particles are the products of the reduction of AgSt + BiOSt compositions (Fig. 4). The X-ray diffraction patterns of the reduction products only show reflections from silver and bismuth metals;

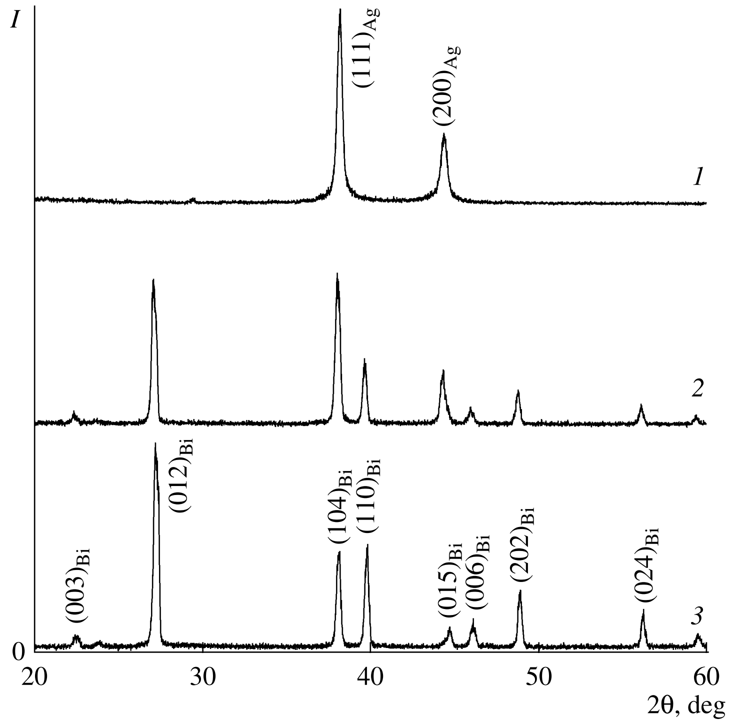

Fig. 4. X-ray powder diffraction patterns for silver–bismuth alloy particles produced by the reduction of stearates in benzyl alcohol. The bismuth concentration (at. %) is (*1*) 1.58, (*2*) 34.5, and (*3*) 94.0.

the intensity of these reflections is affected by the Bi : Ag proportion in the metal stearate batch.

Our investigation allows us to conclude that the reduction of mixtures of bismuth and silver carboxylates is a promising route to submicron-sized bismuth–silver alloys.

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