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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Chemical Synthesis of Tungsten–Copper Nanocomposite Powder[1]

M. Babapour Naseri, A. R. Kamali, and S. M. M. Hadavi

Department of Materials, Malek Ashtar University of Technology, Tehran, Iran

e-mail: m.babapour.naseri@inbox.com

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Abstract—In this study homogeneous powders of $CuWO_4$ and WO_3 was produced from ammonium paratungstate (APT) and copper nitrate. Then, the product was used to prepare nano-sized W-Cu powder. Hence, a mixture of ammonium paratungstate and copper nitrate with predetermined weight proportion was made in distilled water, while the content of the beaker was being stirred at a certain speed to reach the desired composition of W-20 wt % Cu. Mixture was heated to 80–100°C for 6 h. Also, pH range was adjusted at about 3–4. The mixture was then evaporated and dried in the air. To reach W-Cu composite powder, the precursor powders burned out at 520°C for 2 h in the air to form W-Cu oxide powder and then were ball milled and reduced in H_2 atmosphere to convert it into W-Cu composite powder. The resulting powders were evaluated using scanning electron microscopy, X-ray diffraction, thermogravimetric analysis and differential thermal analysis techniques. The results showed that homogeneous powders of W-Cu with particle size of around 100 nm and a nearly spherical shape could be obtained by this process. Each particle include smaller parts with size of around 20-30 nm.

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1. INTRODUCTION

Tungsten-base electrical contacts exhibit excellent resistance to mechanical wear and electrical erosion. Therefore, tungsten-copper (W/Cu) composites, which benefit from the high thermal conductivity of copper, have been used for many decades for applications such as current-carrying contacts, vacuum interrupter, arcing tips, and electrical discharge machining electrodes. Moreover, W/Cu composites benefit from the low coefficient of thermal expansion of tungstate. For this reason they have been recently used as heat sinks, manufactured by powder metallurgy (PM) for microprocessors, microwave modules, wireless telecommunication devices, as well as other power and radio frequency packages for the microelectronics industry. The conventional methods for the fabrication of W/Cu composites are infiltration of a porous tungsten skeleton with liquid copper. Infiltration is a two-step process that wicks molten copper into the open pores of a previously sintered tungsten porous structure. Since copper and tungsten are mutually insoluble, alloying does not occur in the conditions (i.e., pressures and temperatures) usually employed in the infiltration process. Following infiltration, the parts are mechanically machined to the final dimensions. Moreover, the infiltration process does not result in a homogeneous microstructure and it is not a net shape process, thus causing high production costs [1]. In order to reduce costs and to produce net shape components with homogeneous structure, high-density W/Cu parts can be produced by liquid-phase sintering of composite powders characterized by very fine dispersions of both metals [1–3]. Such composite powders can be obtained by the reduction of copper and tungsten oxides [4, 5]. The first step in this process consists in producing cupric tungstate ($CuWO_4$), via solid state reaction of tungstate trioxide (WO_3) or ammonium tungstates (meta,$(NH_4)_6W_{12}O_{39} \cdot xH_2O$ with $0.75 \le x \le 1.25$ or para,$(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$) and copper oxides ($CuO$ or Cu_2O) or copper hydroxide ($Cu(OH)_2$) [6]. After the formation of the cupric tungstate, powders are reduced in flowing hydrogen at 800°C to yield a fine W/Cu composite powder. If the stoichiometric ratio of the starting components is employed, only $CuWO_4$ will be formed, leading to a W/Cu composite powder containing 25.7 wt % Cu. If excess of WO_3 is present in the starting oxide mixture, then metallic powders with lower copper process consists in producing cupric tungstate ($CuWO_4$), via solid state reaction of tungstate trioxide (WO_3) or ammonium tungstates (meta,$(NH_4)_6W_{12}O_{39} \cdot xH_2O$ with $0.75 \le x \le 1.25$ or para,$(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$) and copper oxides ($CuO$ or Cu_2O) or copper hydroxide ($Cu(OH)_2$) [6]. After the formation of the cupric tungstate, powders are reduced in flowing hydrogen at 800°C to yield a fine W/Cu composite powder. If the stoichiometric ratio of the starting components is employed, only $CuWO_4$ will be formed, leading to a

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W/Cu composite powder containing 25.7 wt % Cu. If excess of WO_3 is present in the starting oxide mixture, then metallic powders with lower copper contents can be obtained after the high-temperature reduction step [6]. Currently, ammonium paratungstate (APT) is the dominating raw material used for the manufacture of tungsten-based products. The thermal decomposition of crystalline APT and amorphous ammonium metatungstate (AMT) has been investigated [7, 8]. AMT is a material with good water-soluble tungsten chemicals and larger molecular weight.

At 25°C, the solubility of AMT is 30 g/100 g water, while that quantity for ammonium paratungstate is 1.5 g/100 g water [9]. The decomposition of APT showed that there are two transformations between amorphous and crystalline phases from room temperature to 450°C, that is, precursor (crystalline) ⟶ amorphous powder ⟶ oxides (crystalline) [7, 8]. The aim of the present study is to produce homogeneous powders of $CuWO_4$ and WO_3 from APT and copper nitrate to prepare nano-sized W-Cu powders.

2. EXPERIMENTAL

2.1. Materials and Precursor Synthesis

Experiments were carried out in a glass beaker of 300 ml volume equipped with a mechanical stirrer submerged in a thermostatic bath. Mechanical stirrer (Heidolf RZR 2020) had a controller unit and the bath temperature was controlled using digital controller (within ±0.5°C). Firstly, 150 ml of double distilled water was put into the beaker and when the desired temperature of the beaker content was reached, a predetermined amount of powder with defined size distribution was added into the solution, while the content of the beaker was being stirred at a certain speed of 250 rpm. To fabricate W-20 wt % Cu composite powders, white colored ammonium paratungstate $(NH_4)10W_{12}O_{41} \cdot xH_2O$ powder (>99% purity, Merck, Germany) with mean particle size of 150 μm and blue colored copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, >99% purity, Merck, Germany) were used as raw materials. The beginning mixtures were prepared by mixing APT in an aqueous solution of copper nitrate in distilled water to achieve desired composition of W-20 wt %Cu. APT was slightly soluble and suspended in a stirred reactor containing water. The mixture was heated to 90–100°C for 6 h at relatively constant volume, while maintaining the pH of the slurry at about 3–4 by adding ammonia solution. The volume was maintained constant by adding distilled water. At the end of the reaction, the slurry was evaporated in the air to form a solid powder. The obtained precursor powders were calcined at different temperatures varying between 150 and 750°C for 2 h in the air with a heating rate of 5 K min^{-1}, forming W-Cu oxide powder. The W-Cu oxide composite powder was ball milled for 6 h in the air with a ball/powder weight ratio of 15 : 1. The milling process was carried out in a high-energy ball mill (Fritsch pulverisette-5 model) with the selected rotation velocity of 250 rpm. The ball-milled oxide powder was reduced in an H_2 atmosphere through a two-stage reduction, the first being at the 400°C for 30 min and the second stage of reduction was performed at 650, 700, 750, and 800°C at different times, respectively. The fixed parameter quantities such as stirring speed were selected according to our experiences during the preliminary tests. Notice that since no process which might change the copper content was made, the composition of the powder after synthesis practically remained unchanged and the copper content was identical to its initial content, which was considered stoichiometrically 20 wt %.

2.2. Characterization of the Powders

The thermal decomposition of the precursor powder was studied by measuring the weight loss as a function of temperature in the air using TGA and DTA instruments. The heating rate was 5 K min^{-1} from room temperature to 800°C. The dried precipitates, the calcined precipitates, and the last W-Cu powder were characterized by X-ray diffraction. Particle size and microstructure of the precipitates, calcined, milled, and reduced powders were observed by scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

3.1. Synthesis of W/Cu Oxide Composite Powder

Mixing ammonium paratungstate and aqueous solution of copper was observed to form some colorful precipitate, which once more resulted in the formation of a green precipitate at the end of the reaction. The existence of ammonia was observed in the precipitation, and resulted in the formation of a complex compound. However, when the precipitate is heated to about 100°C, some of the ammonia evaporates. Figure 1 shows diffractogram of the dried precipitates. It indicates that the powder with W/Cu ratio of 4 has a general composition of $(NH_4)_4Cu_3(NH_3)_3H_2W_{12}O_{42} \cdot xH_2O$, in which paratungstate anions are surrounded by copper and ammonium ions, as well as water and possibly ammonia molecules. According to SEM micrograph of the dried precipitates (Fig. 2), it was seen that the precipitates have granular shape with very fine particle size (50–200 nm).

Figures 3 and 4 show TGA and DTA curves of dried precipitates in the air. It is evident from the curves that there are three reaction points for precursor powders in the air atmosphere, which are: 100, 260, and 500°C, respectively. In four steps, different amounts of water and ammonia were released, and different weight losses were obtained. As the first weight loss corresponded to endothermic peaks at 100°C, the weight loss accompanying this step suggests that it can be attributed to loss of physisorbed water. The second decomposition step takes place between 110 and

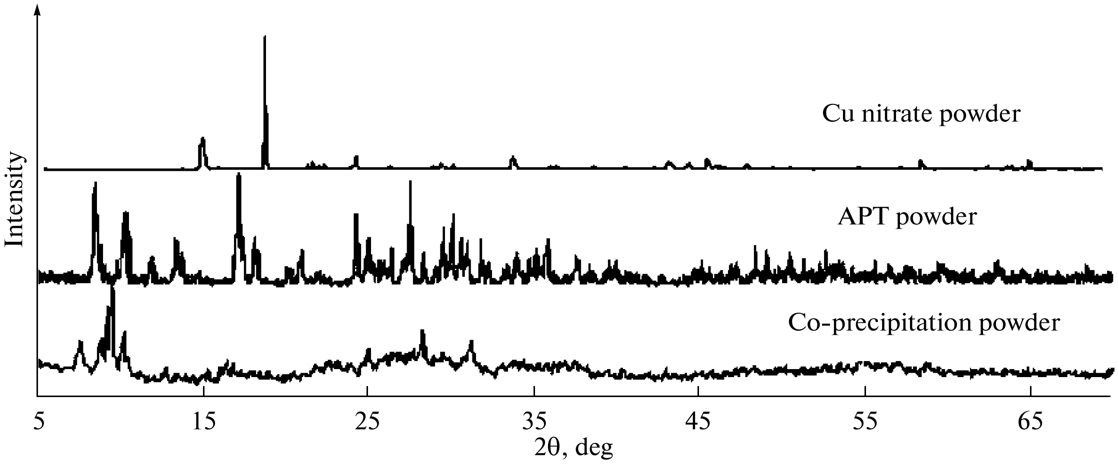

Fig. 1. X-ray diffraction of raw materials (APT and Cu nitrate coprecipitation powder).

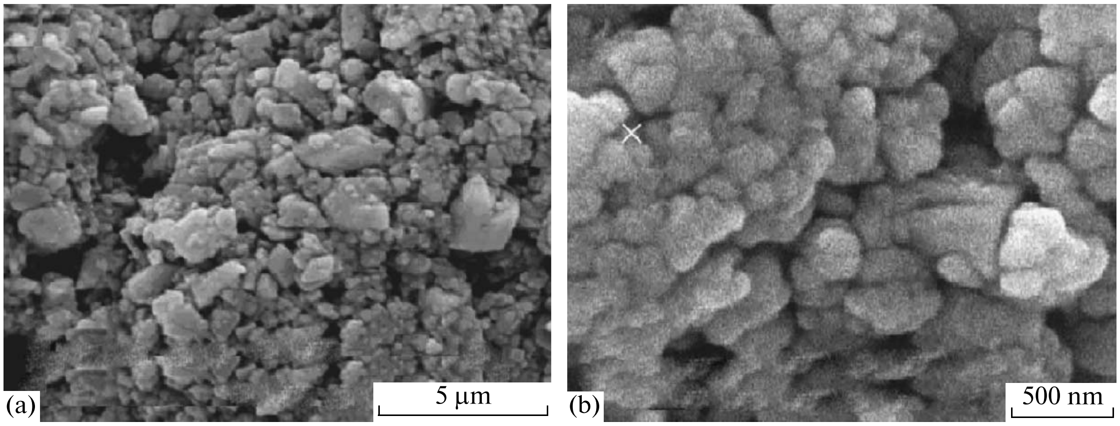

Fig. 2. SEM micrograph of the dried precipitates: (a) 5000×, (b) 30 000×.

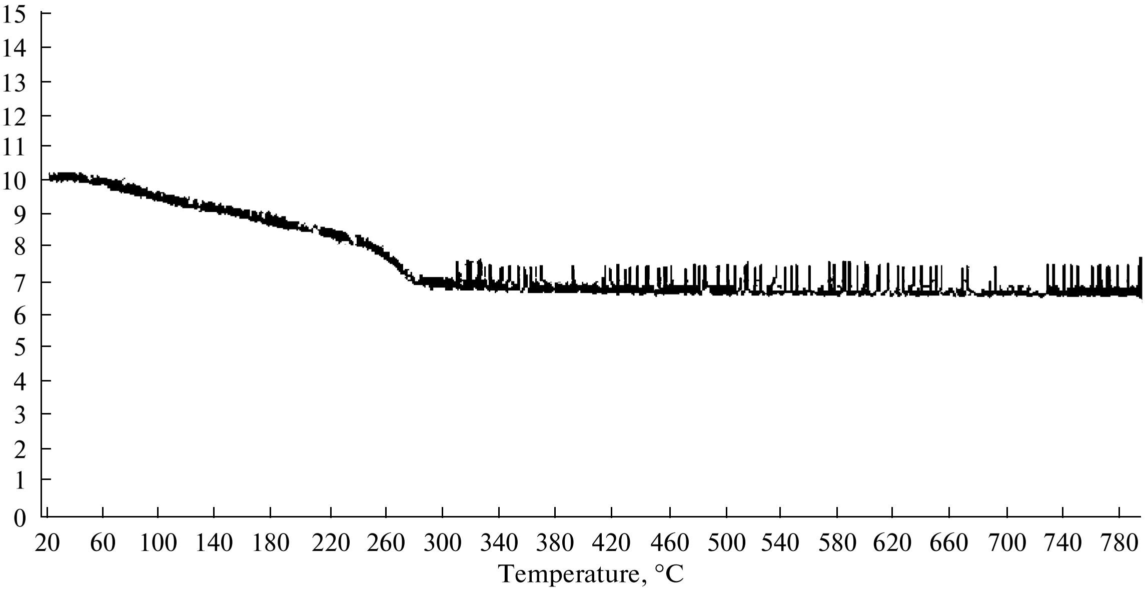

Fig. 3. TGA curve of dried precipitates.

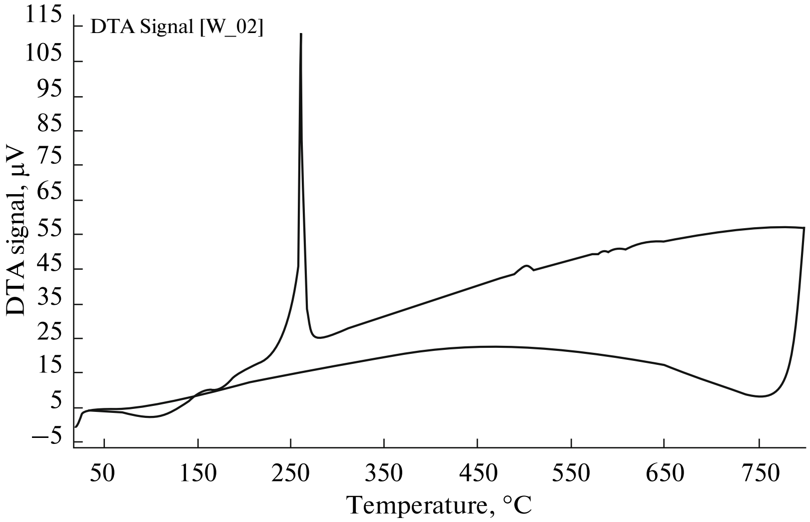

Fig. 4. DTA curve of dried precipitates.

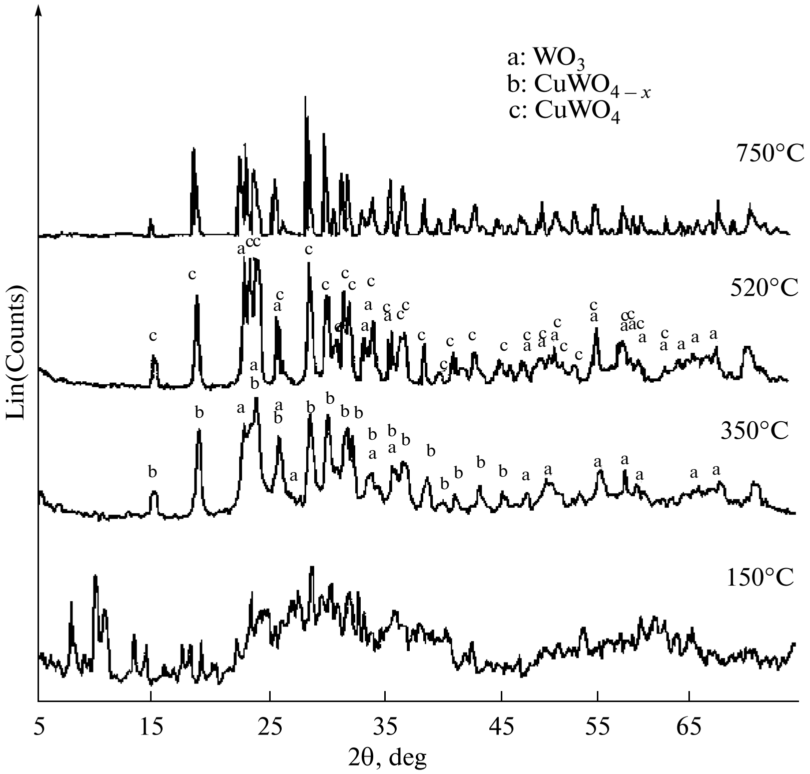

Fig. 5. XRD spectra of the powders calcined at different temperatures.

260°C, and amorphous powder starts to form in this step.

XRD pattern (Fig. 5) of the decomposition product obtained at 150°C, just after the first reaction point, suggests the formation of $(NH_4)_2WO_4 \cdot xH_2O$ and $Cu(NO_2)_2(NH_3)_4$. The third decomposition step (Fig. 3), reached to its maximum at 260°C, is also of exothermic nature. The combustion processes of NH_3 have occurred in exothermic processes at 260°C, producing H_2O, dinitrogen oxide (N_2O), and nitrogen monoxide (NO). The decomposition product obtained at temperature 305°C between second and third reaction points exhibits the diffractogram of $CuWO_{4-x}$ and WO_3. It is seen that $(NH_4)_2WO_4 \cdot xH_2O$ and $Cu(NO_2)_2(NH_3)_4$ phases disappeared and new phases

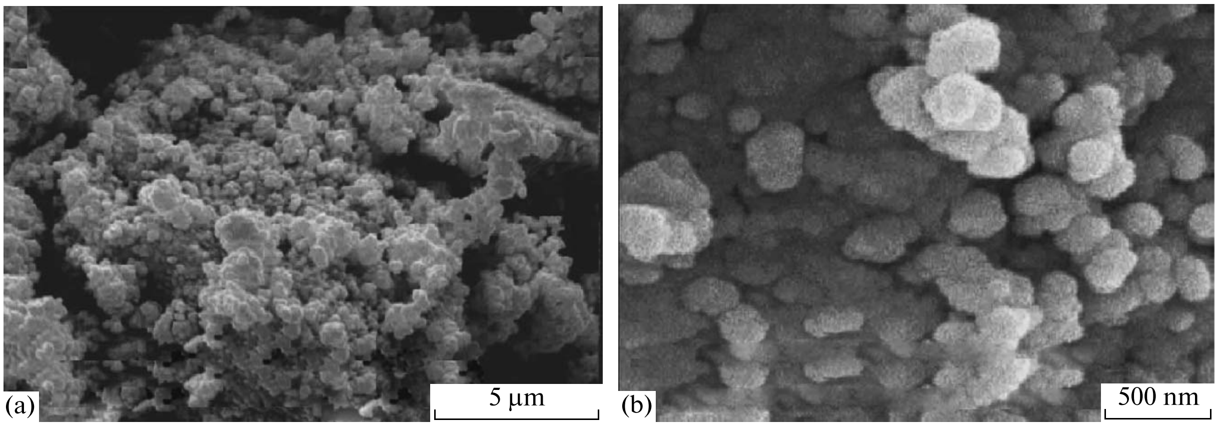

Fig. 6. SEM micrograph of the powder calcined at 520°C (a) 5000×, (b) 30 000×.

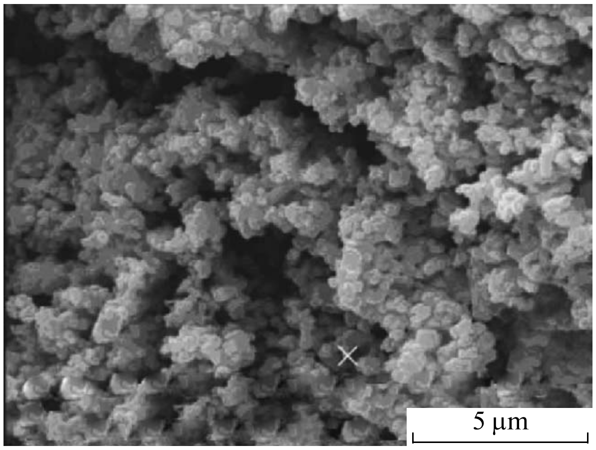

Fig. 7. SEM micrograph of the powder calcined at 750°C.

of $CuWO_{4-x}$ and WO_3 appeared when heated above the temperature of 260°C. In this step, the product was mainly composed of a crystalline powder. The appearance of an amorphous phase has also been identified by XRD. However, very small amount of amorphous phase existed up to 50°C. The peaks of $CuWO_4$ and WO_3 were observed in XRD pattern of the powders calcined at 520°C. At higher temperatures, growing of the crystallites takes place.

Figure 6 shows the SEM micrograph of calcined powders at 520°C, from which could not be seen that the precursor particle has broken into many small particles. The specific surface area decreased due to the agglomeration of small particles during calcinations of the samples at high temperatures and the particles still maintained the shape of the precursor, as shown in Fig. 7. Moreover, as shown in Fig. 6a, the oxidized powders of about 1μm diameter have a highly porous structure owing to removal of organic salt components and oxidation, and still maintained the shell structure of the precursor. It was expected that this shell structure might cause residual pores or Cu pockets in sintered specimen. To avoid this problem, the shell structure was crushed by milling of the oxide powders. Figure 8 shows morphologies of the powders milled in dry condition.

3.2. Preparation of Reduced W/Cu Composite Powder

The ball milled W-Cu oxide powder was effectively reduced in hydrogen atmosphere in a two-stage process minimizing the compositional segregation. Figure 9 shows the XRD patterns of W-20 wt % Cu powders which were fabricated by two stage reduction process at 400°C for 30 min and 650, 700, 750, and 800°C for several times in H_2 (the weight of initial powder was 5 g, and the height of powder bed was 2 mm). Cu oxide completely reduced at 400°C.

As shows in Fig. 10 the optimum temperature for reduction is 750°C in 90 min. Figure 11 shows the microstructure of reduced powders produced from preliminary milled and unmilled oxide powders. As the spherical shell structure was fragmented during ball milling, the reduced powders had a less agglomer-

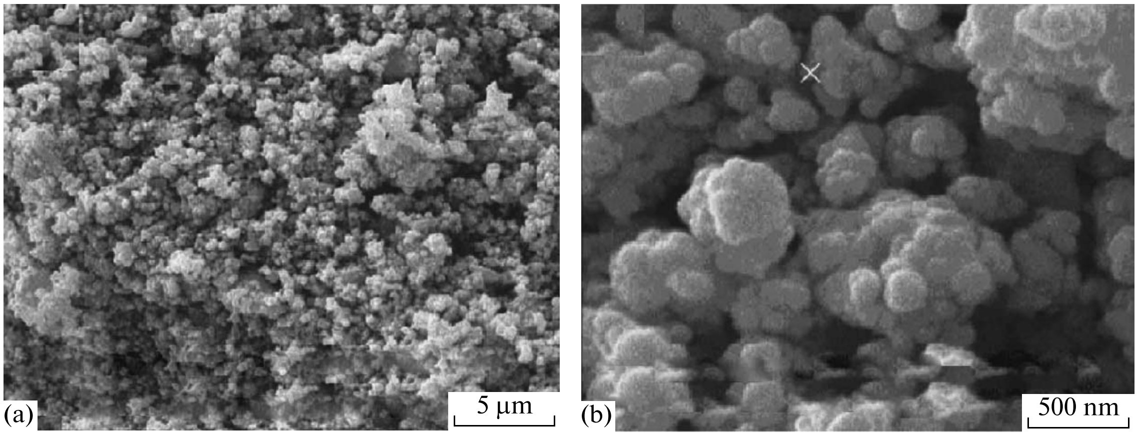

Fig. 8. SEM micrograph of W/Cu oxide powders milled for 6 h in dry conditions.

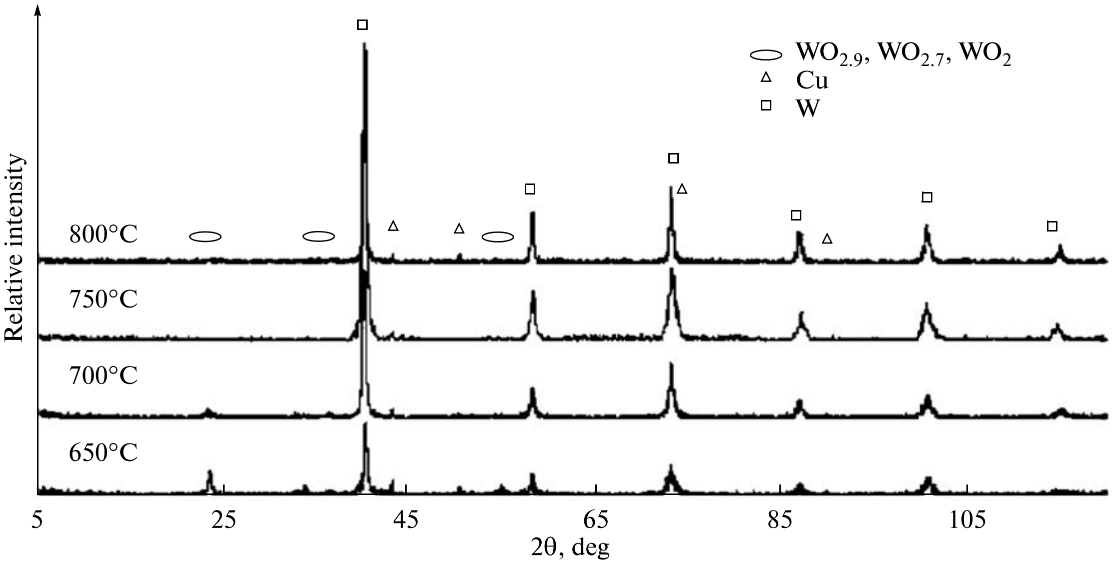

Fig. 9. X-ray diffraction patterns of W-20 wt % Cu powders reduced at different temperatures.

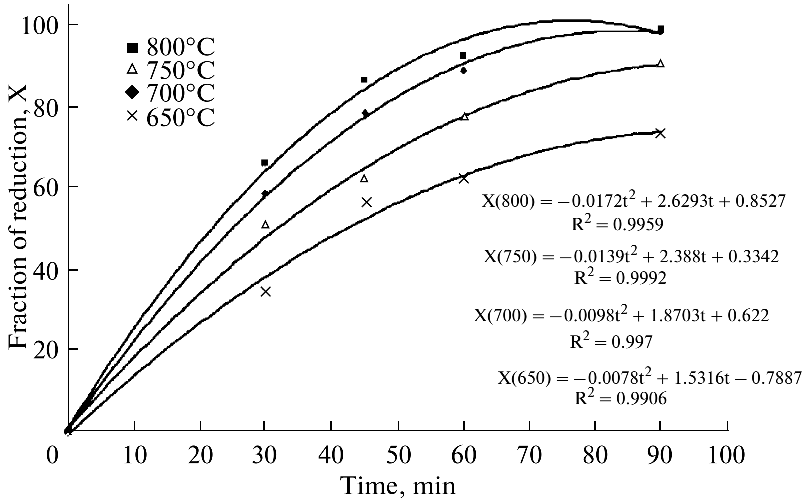

Fig. 10. The fractional conversion, X, as a function of time during the isothermal reduction of oxide powders.

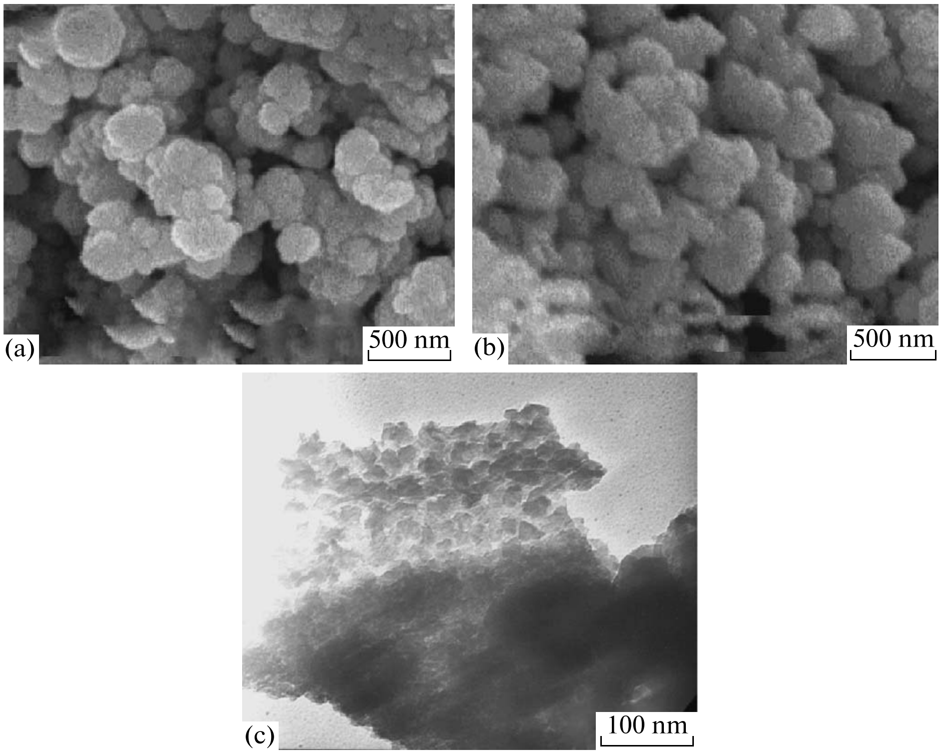

Fig. 11. SEM micrographs of W/Cu composite powders at (a) milled, (b) unmilled conditions, and (c) TEM micrographs of milled sample.

ated structure than those powders without a prior milling. The microstructure of this sample includes particles with size of around 100 nm. As shows in Fig. 11c, each particle include smaller parts with size of around 20–30 nm.

4. CONCLUSION

Based on the investigation made for the fabrication of W-20 wt % Cu composite powder using coprecipitation method, the following points may be highlighted. The W/Cu oxide ultrafine powder with a shell structure could be produced by coprecipitation method from APT and Cu nitrate. Particle sizes of around 80–200 nm have been obtained in the powder calcined at 520°C.The shell structure of oxide powder could be destroyed by ball milling. Ball milling caused reduced agglomerations and better dispersion of the powder. W-20 wt % Cu composite powder with nanosized tungsten particles could be synthesized by reduction of the milled oxide powder.

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