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Preparing Ultradisperse Copper Powder via the Mechanochemical Reduction of Copper Oxides by Magnesium

E. A. Pavlov[a], **T. A. Udalova**[b, c], **T. F. Grigoreva**[b, *], **S. V. Vosmerikov**[b], **I. A. Vorsina**[b], **E. T. Devyatkina**[b], **and N. Z. Lyakhov**[b]

[a] *Gulidov Krasnoyarsk Plant of Nonferrous Metals, Krasnoyarsk, 660027 Russia*
[b] *Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630128 Russia*
[c] *Novosibirsk State Technical University, Novosibirsk, 630073 Russia*
**e-mail: grig@solid.nsc.ru*

Abstract—The mechanochemical reduction of copper (I and II) oxides by magnesium is studied by means of X-ray phase analysis, electron microscopy, and EDS elemental analysis. The conditions for separating copper particles from other products and protecting copper from oxidation during storage are determined. The sizes of the obtained aggregated particles of reduced copper (~100 nm) are estimated via scanning electron microscopy.

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INTRODUCTION

Ultradisperse and nanosized copper powders are widely used in manufacturing new composite materials [1] and as modifiers for polymers, since the specific properties of such particles increase adsorption activity, allowing the production of composite materials with physicochemical, mechanical, and other characteristics that are in demand.

There are many ways to synthesize nano- and ultradisperse materials. Mechanochemical reduction is used for oxidation-reduction reactions with strong exothermic effects [2, 3]. In the mechanical activation of solid mixtures with the grinding of substances, there are an increase in the contact surface area, an acceleration of mass transfer, the deformation mixing of components of mixtures at the atomic level, and the activation of their chemical (mechanochemical) interaction. The practical importance of studying the mechanochemical reduction of metal oxides with the aim of identifying and processing different numbers of objects of mineral and technogenic raw materials cannot be overestimated, since this is quite environmentally friendly.

The use of magnesium as an active metal-reducing agent is subject to its high chemical affinity for oxygen and other nonmetals, with large reserves in the Earth's crust, and the development of technologies for obtaining relatively cheap and pure metal. The reduction of copper oxides using magnesium and by means of mechanical activation has been studied in a number of works [4–6], and for the synthesis of catalysts as well.

The mechanochemical reduction of copper (I and II) oxides with magnesium in order to obtain copper powders is associated with the search for the best conditions for mechanical activation that ensure the course of the oxidation–reduction reaction with the formation of copper and its separation from by-products, the determination of their shape, dimensions, and conditions for protecting against oxidation.

EXPERIMENTAL

Our reagents were copper(I and II) oxides (GOST 16539–79); magnesium powder (GOST 6001–79); hydrochloric acid (GOST 14261–77); sulfuric acid (GOST 14262–78); disodium ethylenediaminetetraacetic acid (EDTA) (GOST 10652–73).

The mixtures of copper oxides and magnesium with various stoichiometric compositions were processed in a high-energy planetary ball mill AGO-2 (drum volume, 250 cm^3; ball diameter, 5 mm; ball load, 200 g; sample batch, 10 g; rotational drum speed around a common axis, 600 and 1000 rpm).

X-ray phase analysis (XRD) was performed on a D-8 Advance Bruker diffractometer.

The morphology of the obtained samples was studied on a Hitachi TM 1000 scanning electron microscope (SEM): accelerating voltage, 15 kV (unchanged); magnification, ×20 to ×10000; maximum viewing area, 3.5 mm^2 (square); sample size, 70 mm (diameter); sample thickness, <20 mm. The microscope was equipped with a TM1000 EDS detector designed for determining the chemical composition of a sample.

RESULTS AND DISCUSSION

The probability of the reduction of copper(I) and (II) oxides by magnesium is determined by the high values of the exothermic effects of these processes:

$$CuO + Mg \rightarrow MgO + Cu; \quad \Delta_r H = -440 \text{ kJ},$$

$$Cu_2O + Mg \rightarrow MgO + 2Cu; \quad \Delta_r H = -430 \text{ kJ}.$$

The diffraction patterns of the original compounds are consistent with the diffraction pattern database PDF-2.

The initial average particle size of magnesium (~200 μm) exceed the average particle size of copper oxides (~1 μm) by more than two orders of magnitude.

During the mechanical activation of a mixture of reagents, there is mechanical melting of magnesium particles (T_m = 650°C) and cladding of copper oxide particles.

CuO–Mg System

X-ray phase study of the effect the duration of mechanical activation and the stoichiometric ratios of the components in CuO–Mg systems (1 : 1 and 1 : 1.5) (Fig. 1) on the degree of copper (II) oxide reduction showed that with activation for 20 s in certain activation regimes there are reduction of copper oxide and oxidation of magnesium. However, the process of CuO reduction in such a short duration of activation does not proceed completely at either 1 : 1 stoichiometry or an excess of magnesium (1 : 1.5). In a system with 1 : 1.5 stoichiometry (Fig. 1, curve *3*) the diffraction pattern (except for Cu_2O and Mg reflections) shows low-intensities reflections that indicate the possible formation of $CuMg_2$ and Cu_2Mg intermetallides according to the phase diagram of the Mg–Cu system. Increasing the activation time to 1 min (Fig. 1, curves *2* and *4*) for stoichiometries of 1 : 1 and 1 : 1.5 results in the disappearance of reflections from intermetallics upon the reduction of copper (II) oxide. The Cu_2O reflections become less intense.

Cu_2O–Mg System

Our studies of the effect the duration of mechanical activation and the stoichiometric ratios (1 : 1 and 1 : 1.5) of the components in the Cu_2O–Mg system showed that with 20 s of activation the reflections of Cu and MgO are recorded on the diffraction patterns of the samples. As in the case of CuO, the reduction of copper oxide in such a short activation time does not proceed completely as with a stoichiometry of 1 : 1, or with the excess of magnesium (1 : 1.5). In the system with a stoichiometry of 1 : 1.5 diffraction patterns show, in addition to Cu and MgO reflections, the reflections of intermetallides $CuMg_2$ and Cu_2Mg, just as in the CuO–Mg system.

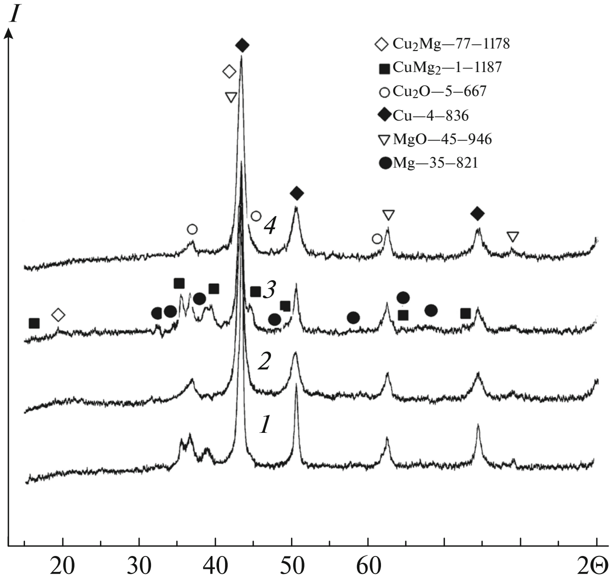

Fig. 1. Diffraction patterns of activation products: (*1, 2*) CuO + Mg stoichiometry 1 : 1; (*3, 4*) stoichiometry 1 : 1.5; (*1, 3*) τ_a = 20 s; (*2, 4*) τ_a = 1 min.

With the reduction of copper oxide (I), increasing the activation time to 1 min (stoichiometry 1 : 1) results in the disappearance of intermetallide reflections. In the system with a stoichiometry of 1 : 1.5, the intensity of intermetallide reflections falls when the activation time is increased to 1 min but they do not disappear. At the same time, the Cu_2O reflections become noticeably less intense, but they too do not disappear, as at stoichiometries of 1 : 1 and 1 : 1.5.

According to [3], the adiabatic temperatures (T_{ad}) for the reactions of CuO and Cu_2O reduction by magnesium are 4531 and <4100 K, respectively. Heats of formation $\Delta_f H^\circ_{298}$ (CuO) = 160 and $\Delta_f H^\circ_{298}$ (Cu_2O) = 175 kJ, respectively. The heats of copper oxide reduction should be close, but the additional copper atom increases the heat capacity and reduces the adiabatic temperature proportionally. The ignition time (τ_{ig}, s) for Cu_2O should thus be longer than that for CuO [2, 3]. However, this difference is almost imperceptible when we compare the results from our X-ray phase analysis of the reduction of copper(II) and (I) oxides with magnesium at the same stoichiometries and activation times.

It follows from our analysis of the diffraction patterns (Fig. 2) of the samples with the stoichiometric composition of copper oxides and magnesium (1 : 1.1) that upon activating the CuO + Mg mixture for 1 min weak reflections of copper oxides were recorded on

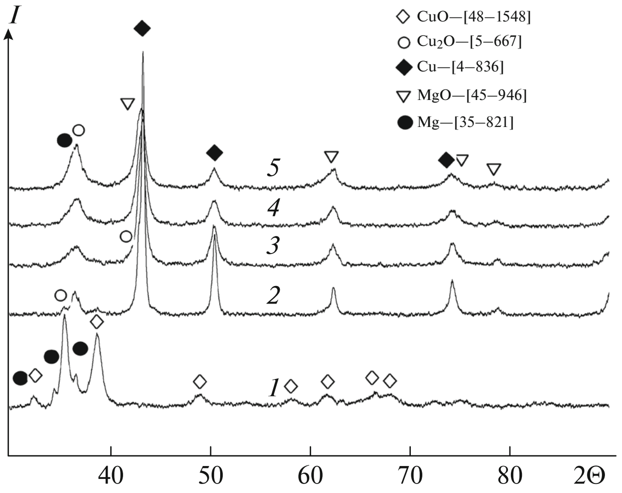

Fig. 2. Diffraction patterns of products of mechanical activation: CuO + Mg system: τ_a = (*1*) 20 s, (*2*) 1 min, (*3*) 2 min, (*4*) 4 min, (*5*) 8 min. Stoichiometry, 1 : 1.1.

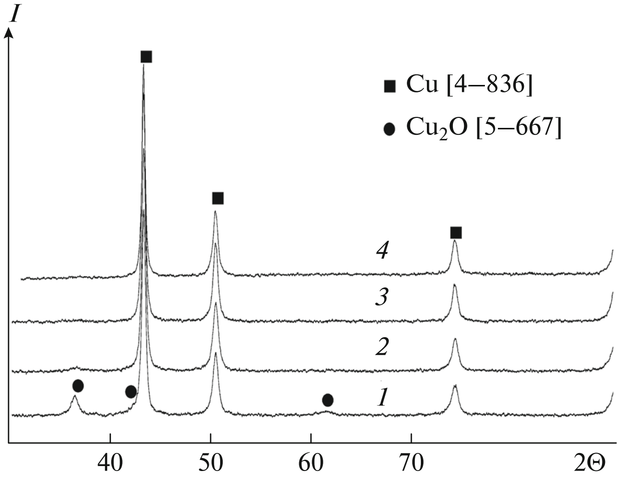

Fig. 3. Diffraction patterns of ultradisperse copper powders after treatment: (*1*) 0.5 M H_2SO_4 and H_2O (298 K); (*2*) 1 M HCl and H_2O (343 K); (*3*) EDTA, H_2O, acetone (343 K); (*4*) stored for 3 months.

the diffraction patterns. In the Cu_2O + Mg system, reflections of Cu_2O were recorded. Increasing the activation time to 2 min allowed the production of samples with copper as the main product, along with magnesium oxide and small amounts of copper oxide as by-products. No intermetallides were in this case recorded using X-rays, and the intensity of copper(I) oxide reflections was minimal. Upon increasing the activation time to more than 2 min, the intensity of reflections of copper(I) oxide and magnesium oxide grew somewhat.

The possibility of separating copper from the by-products of reduction was studied using samples of the mechanochemical reduction of copper(I) and (II) oxides by magnesium with stoichiometric ratio (1 : 1.1) under standard conditions at an activation time of 2 min.

The dependence of the solubility of magnesium oxide on the concentration of hydrochloric and sulfuric acids and temperature [7] allowed us to effectively separate copper upon treatment with 1M HCl at 340–350 K for 30 min with the formation of highly soluble $MgCl_2$. Small amounts of Mg_2Cu or Cu_2Mg intermetallides are also eliminated in treating mechanocomposites with a hydrochloric acid solution. Magnesium is transferred to the Mg^{2+} form in the liquid phase, metallic copper appears in the products of interaction, and no copper ions are detected by qualitative reactions in the solution [8]. In the acid treatment of Cu/MgO mechanocomposite with intermetallide $MgCu_2$, we must therefore consider that the total amount of copper in the powder can be composed of copper both directly reduced in the process of mechanical activation and due to the transfer of copper from intermetallic compounds.

In atmospheric oxygen at temperatures below 423 K and a partial oxygen pressure of 21.28 kPa, the oxidation of copper powders proceeds with the formation of a copper oxide film on the surfaces of the copper particles in which Cu_2O predominates. Under such conditions, virtually no CuO is formed on the surfaces of copper particles (its content passes through a maximum at 573–773 K) [9]. It should be noted that treatment with hydrochloric acid solution allows the partial transfer of Cu_2O into the solution in atmospheric oxygen, with the formation of highly soluble $CuCl_2$.

Two variants of acid treatment for 30 min are proposed for separating finely dispersed copper powder from reduction by-products (magnesium oxide, copper(I) oxide): (1) 1 M HCl (343 K); (2) 0.5 M H_2SO_4 (298 K), followed by washing with distilled water and acetone. However, it is not possible to separate copper from Cu_2O under standard conditions with treatment using 1 M hydrochloric (Fig. 3, curve *1*) or 0.5 M sulfuric acid with subsequent washing with water. Increasing the time of contact between copper powder and water increases the intensity of Cu_2O reflections. In atmospheric oxygen at temperatures of 298 and 343 K, Cu_2O reflections are preserved on the diffraction patterns, along with copper reflections.

To remove copper(I) oxide and keep the copper powder from oxidation after washing with water, we introduced treatment alternately with a solution of disodium salt of ethylenediaminetetraacetic acid [10], water, and acetone (Fig. 3, curve *3*). The diffraction patterns of ultradisperse copper powders after such treatment do not change when the samples are stored for at least 3 months under standard conditions (Fig. 3, curve *4*).

CONCLUSIONS

Our results from electron microscopic studies show that after separation from by-products and stabilization, copper powders consist of aggregates of almost spherical primary particles with dimensions of ~100 nm. These are part of secondary particles, i.e., aggregates 0.2 to 2 μm in size. Energy-dispersive X-ray spectroscopy (EDS analysis) shows that the content of Mg in copper powders does not exceed 2%.

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