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Original Research Paper

Mechanosynthesis of nanostructured composites copper-fullerite, copper-graphite

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ABSTRACT

Comparative studies of the influence of carbon allotropic form on the formation of the structural-phase composition of copper-based composites have been performed by means of Scanning Electron Microscopy, X-ray and Thermal analysis and Raman spectroscopy. It has been stated that the kinetics of solid state reactions in the systems Cu-$C_{60/70}$ and Cu-C_g obtained in process of mechanosynthesis depend on deformational stability and oxidation-reduction properties of fullerite and graphite. It has been shown that partial destruction of fullerene molecules in the Cu-$C_{60/70}$ sample results in the formation of an amorphous fullerite-like phase, copper oxide Cu_2O, and supersaturated solid solution Cu(C, O). Total destruction of fullerene molecules in the system Cu-$C_{60/70}$ results in the formation of supersaturated solid solution Cu(C), just like in the case of the composite Cu-C_g.

1. Introduction

Due to high ductility, electrical and thermal conductivity, antifriction and other properties copper-based materials are widely used in electronics, electrical engineering, machine building and tool engineering [1]. However in many applications they need a considerable improvement of their mechanical characteristics, corrosion stability and high-temperature stability. It is achieved by the synthesis of copper-based composites with the addition of other metals, carbides and some oxides [2–7]. At the same time the electrical conductivity decreases when alloying elements are introduced into copper due to the formation of solid solution.

Special attention is focused on the studies of copper-carbon composites because of good conductivity of both constituents, which makes it possible to use graphite-copper materials as current-collecting elements of sliding electrical contacts. At the same time, the search is on for the improvement of the performance characteristics such as wear resistance and tracking resistance, with a simultaneous reduction of wear rate of the copper counter body of the contact wire [8]. To reducing the cost, it is regarded a possibility of the replacement of silver-containing electric contacts in low-voltage electric devices [9]. Besides, copper-carbon composites can find application as materials for heatsinks in electronic components, where high thermal conductivity and low thermal-expansion factor are the main requirements. The two latter parameters provide the increase of heat dissipation and minimization of thermal loads and deformations, which are dominant factors at packaging of microprocessors, power semiconductors, powerful laser diodes, and micro-electro-mechanical systems [10].

On the other hand, an ultra-fine grain copper presents low thermal stability, requiring the presence of particle dispersions with limited solubility to delay coarsening by grain boundary pinning. Therefore, a promising trend is copper modification with nanocarbon materials such as fullerites. Chemical stability, high strength, high hardness, impact resistance, thermal conductivity, and electrical conductivity [11–13] characterize fullerene molecules, together with nanoscale geometry. This makes fullerites good candidates for dispersion-reinforcing phase without the loss of electrical conductivity. To solve the problem of thermodynamic stability of nanostructured materials it is suggested that fullerites are used as a component that prevents copper recrystallization and increases its strength characteristics [14].

However, the synthesis of copper-carbon composites is hindered by mutual insolubility of carbon and copper. Having dramatically different atomic radii, $r_X/r_A = 0.71$ (the critical ratio, at which interstitial solid solutions are formed, makes up: $r_X/r_A = 0.59$, where X- interstitial element, A – solvent element [15]), the ele-

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ments have different structural types (FCC for copper, and HCP for graphite).

Mechanochemical synthesis (MS) is one of the most promising methods used to extend the limits of equilibrium solid solubility [16]. According to a number of publications, during MS of Cu-$C_{graphite}$ system, owing to deformation-induced atomic mixing, the solubility of carbon in copper extends to 28.5 [17], 25 [18], and 18 [19] at.%. However, the available experimental data for this system are incomplete. The main disadvantages are the following problems:

- The authors mainly focus on the investigation of end products, without giving due attention to phase evolution, mechanisms and kinetics of the transformations in process of copper-graphite composite mechanosynthesis.
- No analysis is also given to the possible interaction of the samples with adsorbed oxygen and milling body wear products.
- With regard to establishing the differences in the formation of the structural-phase composition of mechanocomposites, it would be important to perform comparative studies of the mechanical alloying of copper with fullerites and graphite at similar experimental conditions. In studying these systems, it is important to consider the deformation-induced changes of the structure of carbon materials in the composition of powders.

This work is devoted to the investigation of above-mentioned problems. Detailed study of the initial stage of the solid state reaction during mechanical alloying allows to understand the mechanisms of their flow at the microscopic level.

2. Materials and methods

Copper powders (99.5%), graphite C_g (mechanically crushed rods with a total content of impurities 5×10^{-3} %), and fullerite $C_{60/70}$ were taken as initial materials for mechanical alloying. Copper powders had a dendrite structure formed by spherically shaped particles ~3 to 5 μm in size, with dendrite branches as long as ~150 μm. Fullerite $C_{60/70}$ and graphite particles were of a flat and layered ellipsoid shape, respectively, and had a size of ~100 to 200 μm.

The $C_{60/70}$ mixture was prepared in the Physico-Technical Institute of UrBr RAS by electric-arc evaporation of graphite rods and subsequent extraction of fullerenes from fullerene-containing soot with boiling toluene in a Soxhlet apparatus (extractor), and the following fullerite crystallization from the solution in a rotary vacuum evaporator. The composition of the mixture $C_{60/70}$ was determined with a high-performance liquid chromatograph Agilent 1100 equipped with a diode array detector (chromatographic column Cosmosil Buckyprep 4.6 × 250 mm; toluene as eluent, 1 ml/min, wavelength 290 nm) and was as follows: 82.18% C_{60}; 14.08% C_{70}; 2.81% $C_{60}O$, $C_{60}O_2$ and $C_{70}O$; 0.93% C_{76}, C_{78}, C_{82}, C_{84}. The content of residual toluene according to Thermo Gravimetrical Analysis (TGA) was 1.1%.

The composites Cu-$C_{60/70}$ and Cu-C_g (in proportion Cu-25 at.% C, 30 g by weight) were prepared by mechanosynthesis in planetary ball mill AGO-2S in inert atmosphere P_{Ar} = 0.1 MPa, with drums made of hardened stainless steel, and balls 8 mm in diameter made of ball-bearing steel. The rotation speed of disc and vial were 890 and 2050 rpm, respectively. A stepwise mode of sample preparation was used. A portion of the powder was selected for analysis after some specified time of mechanical milling, and then the remaining part was subjected to further MS. For the investigation of structural evolution with milling time, samples were milled for the periods of 0.5, 1, 2, 4, 6 and 8 h.

The Scanning Electron Microscopy (SEM) observations were carried out on Quanta 200 3D apparatus equipped with an Energy Dispersive X-ray spectroscope Pegasus EDAX operated at 120 eV. Prior to analysis, the powder was applied on an electro-conducive scotch tape.

X-ray studies were performed with a diffractometer BRUKER D8 ADVANCE (CuKα radiation). To clarify the parameters of copper crystal structure, full-profile analysis was performed using computer software TOPAS 4.2. The lattice parameter was determined using (1 1 1), (0 0 2), (2 0 2), (1 1 3), (2 2 2) copper reflections. Magnesium oxide (MgO), prepared according to the description in [20], was taken as an X-ray standard to account for apparatus broadening. The error in lattice parameter calculation (a_{Cu}) was no >0.0002 Å, crystalline sizes (L) – 0.5 nm, microstrains level ($\langle\varepsilon^2\rangle^{1/2}$) – 0.05%.

Raman spectroscopy (RS) was used to study the structural changes of carbon in mechanocomposites Cu-$C_{60/70}$ and Cu-C_g. The spectra were taken with a spectrometer Labram HR800 (HORIBA) with the laser wavelength λ = 632.81 nm.

Thermal analysis of powders before and after milling was carried out on a TGA/DSC STD Q600 thermal analysis system.

3. Results

3.1. Structural-phase composition of mechanocomposites Cu-$C_{60/70}$ and Cu-C_g

Fig. 1 shows X-ray diffraction patterns of Cu-$C_{60/70}$ and Cu-C_g powders prepared at t_{MS} = 1, 2 and 8 h. Typical of both systems is

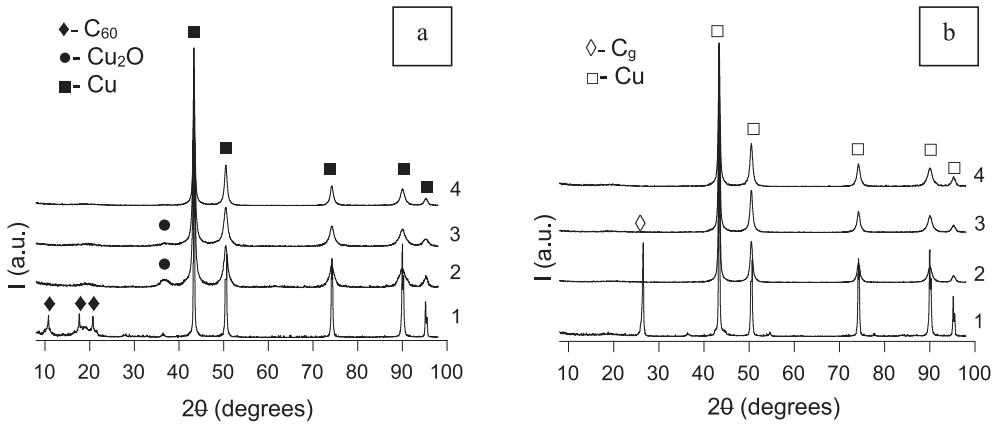

Fig. 1. Diffractograms of Cu-$C_{60/70}$ (a) and Cu-C_g (b):**1** initial, **2** after 1 h MS, **3** after 2 h MS, **4** after 8 h MS.

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