NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2016, 7 (1), P. 190–197

The influence of carbon (fullerite, graphite) on mechanical alloying of Cu-25 at % C composites

R. M. Nikonova, V. I. Ladyanov, N. S. Larionova

Physicotechnical Institute, Ural Branch of Russian Academy of Sciences, Izhevsk, Russia

RozaMuz@ya.ru

PACS 61.48.-c, 61.72., 63.22. Kn, 68.35.-, 78.30.Na, 81.05.ub, 81.07.Bc, 82.80.Gk

DOI 10.17586/2220-8054-2016-7-1-190-197

A comparative study of Cu-$C_{60/70}$ and Cu-C_g composites obtained by mechanical alloying has been performed by means of scanning electron microscopy, X-ray diffraction, and Raman spectroscopy. It has been demonstrated that high stress-related effects, which take place during the mechanochemical synthesis of Cu- $C_{60/70}$ and Cu-C_g composites with a nanocrystalline structure, result in the formation of an oversaturated solid solution of carbon in copper, Cu(C). The morphology and the parameters of the crystal lattice $a_{Cu}(t_{MA})$ and the sizes of the crystallites $L(t_{MA})$ of the powders obtained depend on the deformational stability of fullerite and graphite and also on their reactivity to adsorbed oxygen.

Keywords: fullerite, graphite, copper, mechanically alloyed composites.

Received: 20 November 2015

1. Introduction

At present many of researchers' attention is devoted to investigations on the preparation of nanostructured materials for engineering and functional purposes and on the optimization of their physical and technological properties. An upcoming trend here is the synthesis of metal matrix composites modified by carbon nanomaterials (fullerenes, carbon nanotubes, etc.), which have unique physical and mechanical properties.

One of the most widely commercially applied metals is copper – manufacturers like it for its high electrical and thermal conductivity. However its low hardness, and low corrosion resistance limit its use in pure form. To improve its structural characteristics, researchers suggest considering the prospects of preparing of copper-carbon composites. Carbon can protect copper from oxidation and/or regenerate its already oxidized surface. Also, the problem of electrochemical copper erosion can be resolved.

Different carbon forms are used to prepare the Cu-C composites. In most cases, graphite can be utilized [1, 5-8]. Nanotubes [9-13], nanodiamonds [2,5], and fullerites [3, 14-16] are mentioned in the literature as possible carbon sources. Among the methods used for modification of copper with carbon are sintering [6, 13], the formation of film coatings by the joint deposition of Cu and carbon [15, 16], carbon deposition from gaseous phase via the catalytic decomposition of acetylene and ethylene with subsequent compacting and sintering [12], application of ultra-high strain [1], and shock-wave loading [14]. Also, a promising technique is mechanical milling in high-energy ball mills [2,3-5,7]. u-C specimens have higher hardness than that of carbon-free copper [8,12], which is attributed primarily to the stabilization of copper grain boundaries [8].

Since under equilibrium conditions carbon is practically insoluble in copper, mechanochemical synthesis (MS) is considered a promising method for the preparation of such composite materials – it provides the atomic-level mixing of components and thus increases solubility.

Since different forms of carbon have different physico-mechanical and -chemical properties, it is expected that mechanical alloying (MA) of composites with their addition will give different results. In this regard, it would be especially interesting to conduct comparative studies on the effect of allotropic forms of carbon on the formation of the structure of copper-based composites.

So far, comparative studies on the mechanical alloying of copper together with fullerites and graphite have not been performed. However, the authors in [3] assume that the synthesis of composites with fullerene particles in a copper matrix will give better results. The investigations of Fe-C, Al-C, Mg-C systems in papers [14-16] confirm that in contrast with graphite, fullerenes do exert a more significant strengthening effect both immediately after mechanical alloying [16] and after the following spark plasma sintering [14,15].

In this paper, we present the results for the comparative study of mechanically alloyed copper-fullerite and copper-graphite composites.

2. Materials and methods

Copper powders (99.5 %), graphite C_gACS (mechanically crushed rods), and fullerite $C_{60/70}$ were taken as elemental powders for mechanical alloying. Copper powders had a dendrite structure formed by spherically-shaped particles $\sim$ 3 – 5 μm in size, with dendrite branches as long as $\sim$ 150 μm (Fig. 1, 0 h MA). Fullerite $C_{60/70}$ and graphite particles were of a flat and layered ellipsoid shape, respectively, and had a size of $\sim$100 – 200 μm. The composition of $C_{60/70}$, according to HPLC and thermal gravitational analysis, 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} %; 1.1 % of residual toluene.

For copper-fullerite and copper-graphite composites, the copper and carbon powders were mixed in the proportion Cu-25 at % C (hereafter referred to as Cu-$C_{60/70}$ and Cu-C_g, respectively) with the total weight of 30 g. The samples were mechanically alloyed in a planetary ball-mill AGO-2S (balling drum material was hardened stainless steel, balls 8 mm in diameter were made of ball-bearing steel) in a pre-evacuated inert atmosphere $P_{Ar} = 0.1$ MPa ($P = 10^{-3}$). The duration of mechanical alloying ranged from 15 min to 8 h.

A BRUKER D8 ADVANCE (CuKα radiation) diffractometer was used to perform X-ray diffraction study of the samples. Magnesium oxide (MgO), prepared as described in [17], was taken as a reference specimen to account for instrument broadening. The calculations were made with an error for lattice parameters (a_{Cu}) smaller than 0.002 Å, crystallite sizes (L) 0.5 nm, and the level of microdistortions ($\langle\varepsilon^2\rangle^{1/2}$) 0.05 %. To measure the changes in particle morphologies (size and shape) a scanning electron microscope QUANTA 200 3D was used. Raman spectroscopy was used to study the structural changes of carbon in the mechanically alloyed Cu-$C_{60/70}$ and Cu-C composites. The measurements were taken with a Labram HR800 (HORIBA) spectrometer with an exciting laser wavelength $\lambda = 632.81$ nm.

3. Results and discussion

Fig. 1 includes microimages of the initial copper powders and Cu-$C_{60/70}$ and Cu-C_g samples, and also the images taken after their mechanical alloying for 1 and 8 h. It is seen that in the process of mechanical alloying of copper-carbon powders, different deformation kinetics of Cu-$C_{60/70}$ and Cu-C_g composites are observed, depending on the carbon form. This follows from the different shapes of the resultant particles and their dispersion. After 1 h of milling, the particles of the mechanically alloyed composites represent stone-like agglomerates formed from smaller particles (Fig.1), with Cu-$C_{60/70}$ powders being more finely-dispersed at the beginning

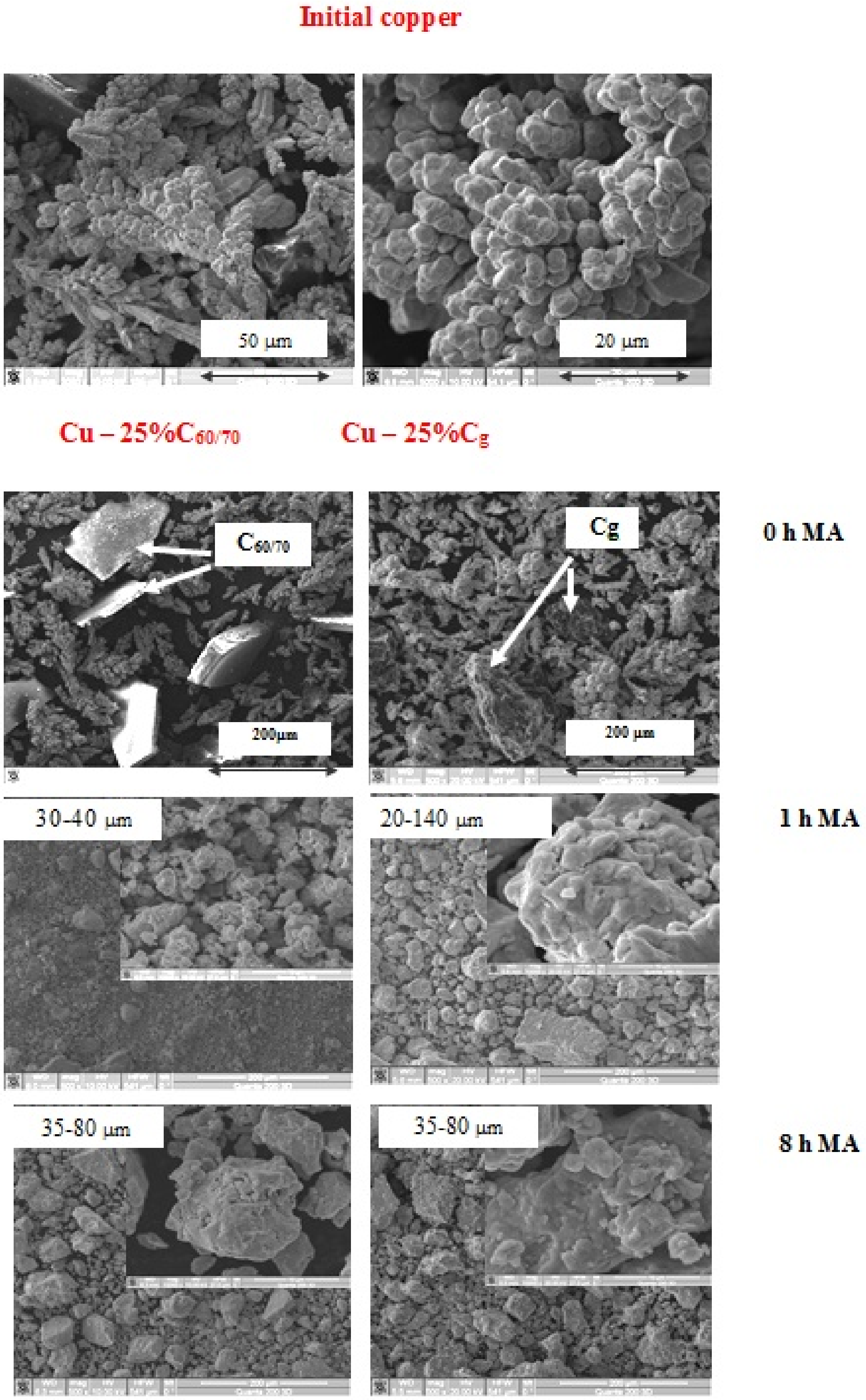

FIG. 1. SEM-images of particles of Cu-25 %C powders in their initial state and after 1 and 8 h of mechanical alloying

than Cu-C_g powders. With an increase of the mechanical alloying time to 8 h, the particle sizes in the composites compared tend to level off (Fig. 1). It should be noted that with a decrease in the composites' carbon content (to 5 at %), the morphological differences become more expressed.

Figure 2 demonstrates X-ray diffraction patterns for Cu-$C_{60/70}$ and Cu-C_g powders that were mechanically activated for 0.5, 1, 2 and 8 h (t_{MA}). Judging by the appearance of an X-ray amorphous halo in the area of $C_{60/70}$ main reflections at angles $2\theta = 8 - 35$ ° (Fig. 2a, insert) an amorphous fullerite-like phase is formed in the Cu-25 % $C_{60/70}$ blend after its mechanical alloying for 0.5 – 2 h. At the same time, Cu_2O is formed. As concerns Cu-C_g, after as early as 0.5 h of mechanical alloying ($2\theta \sim 26$ °), the structural maximum of graphite in the X-ray diffraction pattern totally disappears; also, the formation of Cu_2O is no longer observed.

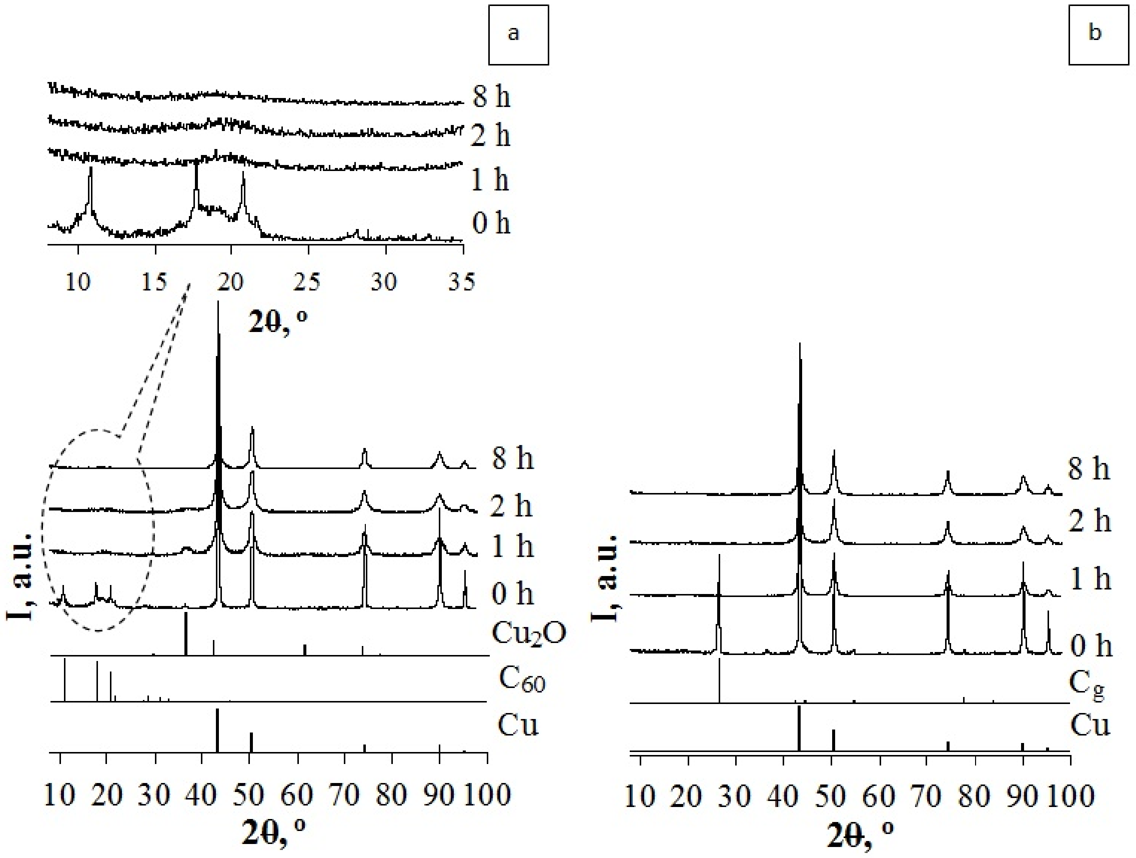

FIG. 2. X-ray diffraction patterns of Cu-$C_{60/70}$ (a) and Cu-C_g (b) powders at different MA times

Figure 3 shows the Raman spectra of Cu-$C_{60/70}$ and Cu-C_g samples after 1 and 8 h of mechanical alloying. Since D-band (1332 cm^{-1}) has a higher intensity in comparison with G-band (1582 cm^{-1}) (Fig. 3, a), we can draw a conclusion that the graphite structure in the Cu-C_g sample after 1 h of mechanical alloying is characterized by a higher number of defects. A considerable intensity decrease and broadening of G-band is a consequence of graphite amorphization [18]. The presence of the main bands of fullerenes C_{60} and C_{70} in the Raman spectra of the $C_{60/70}$ composite mechanically milled for 1 h indicates the presence of fullerenes in the sample (Fig. 3, a). Owing to the spherical shapes of C_{60} molecules, their high compressive strength and weak intermolecular bonds in a crystal, fullerenes in the process of high energy milling presumably act as "molecular bearings" [19]. Due to this, higher dispersion is attained in the process of mechanical alloying of the Cu-$C_{60/70}$ system.

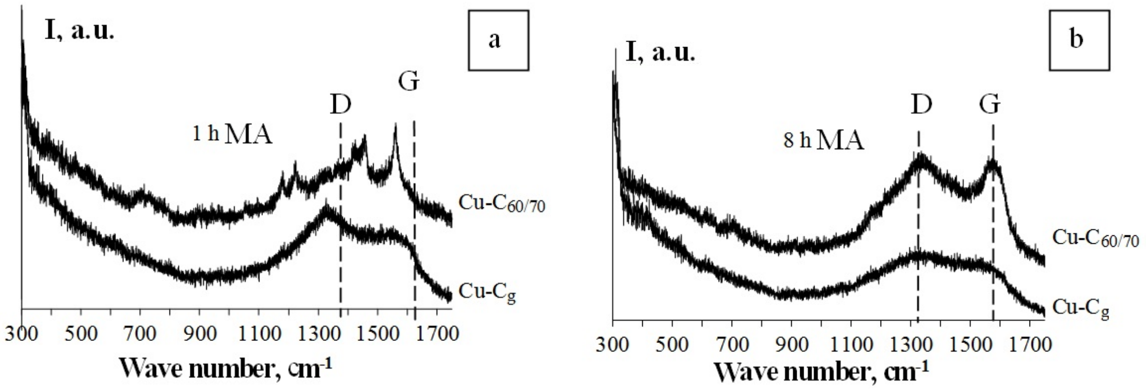

FIG. 3. Raman spectra of Cu-$C_{60/70}$ and Cu-C_g composites after 1 (a) and 8 (b) h of MA

For long periods of mechanical alloying (8 h), the Raman spectra of both Cu-$C_{60/70}$ and Cu-C_g samples correspond to amorphous carbon (Fig.3, b). This is indicative of the destruction of fullerene molecules and the disordering of graphite's lamellar structure. As a result, particle sizes in the compared Cu-$C_{60/70}$ and Cu-C_g systems level off (Fig. 1). It is to be noted that smaller particle sizes in Cu-$C_{60/70}$ powders in comparison with Cu-C_g powders can also be explained by the formation of a fragile copper oxide Cu_2O at $t_{MA} = 0.5 - 2$ h (Fig. 2, a).

Thus, based on the results of Raman spectroscopy, it can be stated that the differences observed in the Cu-$C_{60/70}$ and Cu-C_g systems in process of mechanical alloying depend on a higher deformation stability of fullerite in comparison with graphite. The latter was previously shown in our research [20].

According to the diffraction maxima of the Cu-C sample profiles, the dependences of copper crystalline lattice parameter a_{Cu} and crystalline sizes L on the mechanical alloying time (t_{MA}) for Cu-$C_{60/70}$ and Cu-C_g are different (Fig. 4). At $t_{MA} = 1-2$ h Cu-$C_{60/70}$ powders have smaller grains, 12 nm, in contrast with Cu-C_g powders, at a maximum value of $a_{Cu} = 3.6169$ Å. In the plot of a_{Cu} versus milling time (t_{MA}) we observe the maximum, and in the plot of L versus milling time, the minimum is observed. In the process of milling for 4 – 8 h crystallite sizes increase and reach values close to those for Cu-C_g composites. At the same time, a_{Cu} decreases to 3.6162 nm. The change of grain sizes in the samples is seen to correlate with the scanning electron microscopy data (Fig. 1) for particle dispersion.

In compliance with [21], from a thermodynamics point of view, the presence of adsorbed oxygen at Cu-C interfaces should not have resulted in the formation of copper oxide, since the latter should have been reduced by carbon. However, since the energy of attachment for oxygen atoms to a C_{60} molecule exceeds that of the heat of Cu_2O formation (376.8 and 166.6 kJ/mol, respectively [22,23]), it is energetically favorable for oxygen to react with copper. As a result, copper oxide Cu_2O is formed in the sample, with part of oxygen additionally dissolved in the copper matrix to form Cu(C, O). This explains larger value of $a_{Cu} = 3.6169$ Å in comparison with Cu-C_g ($a_{Cu} = 3.6162$ Å). Furthermore, larger a_{Cu} value in the Cu-$C_{60/70}$ system is also determined by smaller grain sizes $\langle L \rangle$, and hence, larger specific surface area for the particles.

Because of this, the solid phase reactions in the Cu-$C_{60/70}$ system proceed in two steps. At the beginning (within 2 h) copper oxide (Cu_2O) is formed, with fullerene molecules remaining uninvolved. At the same time, an oversaturated solid solution of carbon and oxygen

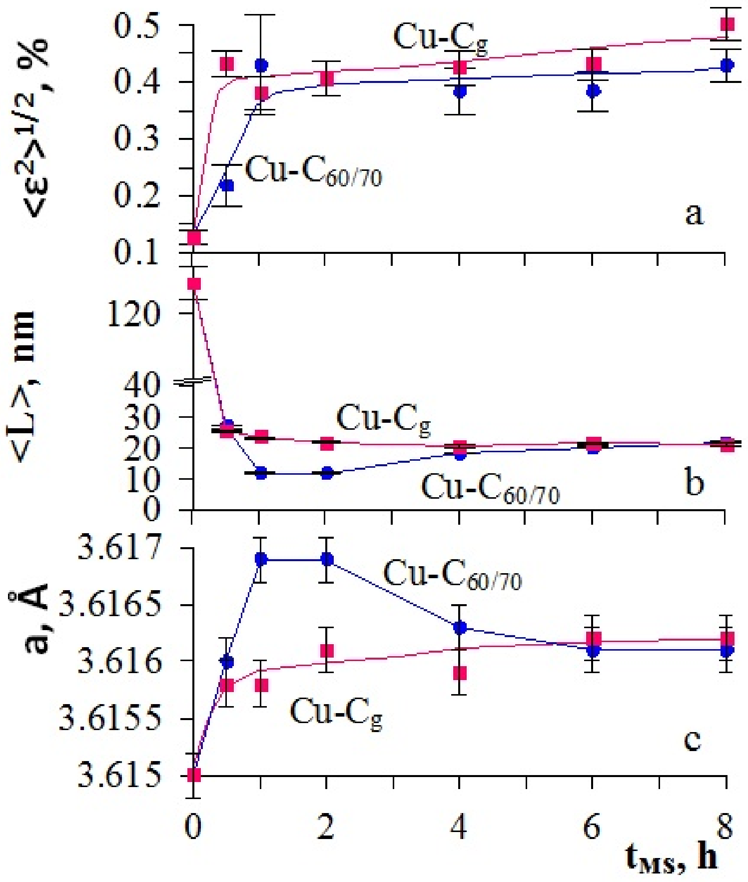

FIG. 4. Dependence of microstress (a), crystallite sizes (b), and lattice parameter (c) of copper in composites Cu-$C_{60/70}$ and Cu-C_g on MA time

in copper Cu(C, O) is formed. The second stage is initiated by the destruction of fullerene molecule frameworks caused by high energy deformation. This results in amorphous carbon formation. At 4 – 8 h of MA, the formed copper oxide is reduced:

$$2Cu_2O + C \rightarrow 4Cu + CO_2 \uparrow -Q$$

and a partial diffusional decay of the oversaturated solid solution Cu(C, O) occurs with the formation of Cu(C). This decay can be explained by the reaction proceeding between its components:

$$[C]_{Cu} + [O]_{Cu} \rightarrow CO \uparrow$$

where $[C]_{Cu}$ and $[O]_{Cu}$ are carbon and oxygen dissolved in copper. As a result, an oversaturated solid solution of Cu(C) is formed with $_{Cu} = 3.6161$ Å, and this is accompanied by the recrystallization of the sample ($\langle L \rangle$ increases from 12 to 20 nm).

Unlike the case with Cu-$C_{60/70}$, the mechanical alloying of Cu-C_g is a one stage process. As a result of this process, an oversaturated solid solution Cu(C) is formed. Because of a faster amorphization of graphite and its high reducibility neither oxide formation nor oxygen dissolution in copper is observed here.

Thus, it can be stated that the differences in the dependence a$_{Cu}(t_{MC})$ observed between Cu-$C_{60/70}$ and Cu-C_g at the initial stage of their MA (up to 2 h) are not only determined by the different deformational stability of fullerite and graphite, but also by their different reactivity with oxygen.

4. Conclusion

Regularities of structural and phase conversions in the mechanical alloying processes of copper-fullerite and copper-graphite composites have been identified. It has been demonstrated that the mechanical alloying of Cu-$C_{60/70}$ and Cu-C_g composites with a nanocrystalline structure results in the formation of an oversaturated solid solution of carbon in copper, Cu(C). The formation kinetics of this solution, together with the powder morphology has been shown to depend on the deformational stability of fullerite and graphite, as well as their reactivity with adsorbed oxygen.

Acknowledgements

The work has been carried out under financial support of the program the Presidium of Ural Brunch, RAS (grant 15-20-2-22).

References

[1] Barner A., Mundim K.C., Ellis D.E., Dorfman S., Fuks D., Evenhaim R. Microstructure of Cu-C interface in Cu-based metal matrix composite. *Sensors and Actuators A*, 1999, **74**, P. 86–90.

[2] Sheibani S., Ataie A., Heshmati-Manesh S., Khayati G.R. Role of process control agent on synthesis and consolidation behavior of nano-crystalline copper produced by mechano-chemical route. *Mater. Lett.*, 2007, **61**, P. 3204–3207.

[3] Guillet A., Yama Nzoma E., Pareige P. A new processing technique for copper-graphite multilamentary nanocomposite wire: Microstructures and electrical properties. *J. Mater. Process. Technol.*, 2007, **182**, P. 50–57.

[4] Nunes D., Livramento V., Mateus R., Correia J.B., L.C.Alves, Vilarigues M., Carvalho P.A. Mechanical synthesis of copper-carbon nanocomposites: structural changes, strengthening and thermal stabilization. *Mater. Sci. Engin. A*, 2011, **528**, P. 8610–8620.

[5] Chu K., Gua H., Jia C., Yin F., Zhang Z., Liang X., Chen H. Thermal properties of Carbon Nanotube-Copper Composites for Tremal Management Applications. *Nanoscale Res. Lett.*, 2010, **5**, P. 969–874.

[6] Shukla A.K., Nayan N., Murty S.V.S.N., Sharma S.C., Chandran P. Processing of copper-carbon nanotube composites by vacuum hot pressing technique. *Mater. Sci. Engin. A*, 2013, **560**, P. 365–371.

[7] Yamamoto K., Taguchi T., Hanada K., Osawa E., Inakuma M., Livramento V., Correia J.B., Shohhji N. TEM studies of nanocarbons and nanodiamonds (ND): mechanical milling of ND and Cu. *Diamond Related Mater.*, 2007, **16**, P. 2058–2063.

[8] Medvedev V.V., Popov M.Y, Mavrin B.N., Denisov V.N., Kirichenko A., Tat'yanin E.V., Ivanov L.A., Aksse-nenkov V.V., Perfilov S.A., Lomakin R., Blank V.D. Cu-C_{60} nanocomposite with suppressed recrystallization. *Appl.Phys.A*, 2011, **105**, P. 45–48.

[9] Bezruchko G.S., Razorenov S.V., Popov M.Y. The influence of the admixture of the fullerene C_{60} on the strength properties of aluminum and copper under shock-wave loading. *J. Phys.: Conf. Ser.* 2014, **500**, P. 112008(1-6).

[10] Kovtun V.A. Investigation of structure and properties of composite materials based on copper-carbon nanoparticles powder systems formed by electrocontact sintering. *Machines, Technologies, Materials*, 2012, **3**, P. 34–38.

[11] Shpilevsky E.M., Baran L.V., Okatova G.P. Structurally-phase composition of the films Cu-C_{60}, obtained by condensation in a vacuum of a joint atomic-molecular flow. *Adv. Mater.*, 2003, **3**, P. 56–59.

[12] Larionova T.V., Markina N.V., Petrov N.V., Shapovalov O.S., Afanasev A.A., Koltsova T.S. The structure and hardness of the copper composite materials of carbon. *Vestnik Novgorod State University*, 2012, **68**, P. 15–19.

[13] Guillet A., Nzoma E.Yama, Pareige P. A new processing technique for copper-graphite multifilamentary nanocomposite wire: Microstructures and electrical properties. *J. Mater. Process. Technol.*, 2007, **182**, P. 50–57.

[14] Robles Hernandez F.C. Production and characterization of Fe-Cgraphite and Fe-Cfullerene composites produced by different mechanical alloying techniques. *J. Metallurgy*, 2004, **10**(2), P. 107–118.

[15] Robles Hernandez F.C., Calderon H.A. Nanostructured Al/Al_4C_3 composites reinforced with graphite or fullerene and manufactured by mechanical milling and spark plasma sintering. *Mater. Chem. Phys.*, 2012, **132**, P. 815–822.

[16] Nikonova R.M., Dorofeyev G.A., Ladyanov V.I., Pushkaryov B.Ye. Mechanical alloying of Mg nanocomposites with different forms of carbon. *Chem. Phys. Mezoscopy*, 2010, **12**(3), P. 382–389.

[17] Pratapa S., O'Connor B. Development of MgO ceramic standards for X-ray and neutron line broadening assessments. *Advances in X-ray Analysis*, 2002, **45**, P. 41–47.

[18] Bukallov S.S., Mikhalitzin L.A., Zubavichus Ya.V., Leites L.A., Novikov Y.N. Investigation of the structure of graphite and some other sp^2 carbon materials by means of micro-Raman spectroscopy and X-ray diffraction. *Russian Chem. J.*, 2006, **L**(1), P. 83–91.

[19] Shpilevskiy M.E., Stelmakh V.F. Fullerenes and fullerene-like structures as a basis for advanced materials. *J. Engin. Phys.*, 2001, **74**(6), P. 106–112.

[20] Lad'yanov V.I., Nikonova R.M., Larionova N.S., Aksenova V.V., Mukhalin V.V., Rud A.D. Deformation Induced Changes in the Structure of Fullerites $C_{60/70}$ during Their Mechanical Activation. *Phys. Solid State*, 2013, **55**(6), P. 1319–1324.

[21] Berner A., Fuks D., Ellis D.E., Mundim K., Dorfman S. Formation of nano-crystalline structure at the interface in Cu-C composite. *Appl. Surf. Sci.*, 1999, **144-145**, P. 677–681.

[22] Sidorov L.N., Yurovskaya M.A., et al. *Fullerenes*. Moscow: Publishing House "Exam", 2005, 688 p.

[23] Azarenkov N.A., Litovchenko S.V., Nekludov I.M., Stoyev P.I. *Corrosion and protection of metals. Part 1. Chemical corrosion of metals. Textbook*. Kh.NU, Kharkov, 2007, 187 pp.