Cu-Expanded Graphite Composite Material Preparation and Thermal Properties

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Article info	Abstract
	A composite material based on expanded graphite (EG) and copper compounds was obtained by natural graphite oxidation with 95% nitric acid, copper (II) nitrate and granular carbamide addition with further rapid heat treatment at three different exfoliation temperatures: 800, 1000 and 1200 °C. It was found that the composition of copper containing graphite material depends on the temperature and the atmosphere of thermal expansion. The formation of copper oxides can be eliminated if rapid heat treatment is conducted in nitrogen at 1200 °C. Thermal conductive properties: thermal diffusivity and specific heat capacity of obtained Cu-expanded graphite samples were measured. It was revealed that the dependence of thermal conductivity (TC) of Cu-graphite material has non-linear character in the studied range of copper content. The incorporation of 3% copper into expanded graphite allows to increase its thermal conductivity by 20% while the further Cu content growth leads to the TC decrease from 6 to 4.5 W/(m·K). The specific heat capacity is constant at $\omega(Cu)<3\%$ and reduces in the range (3–8)% Cu. The advantage of proposed technique of Cu-expanded graphite materials preparation is exclusion graphite intercalation compounds hydrolysis step with further drying because of carbamide addition.

1. Introduction

Materials based on expanded graphite have been the subject of scientific interest for many years because of their relatively simple production method and the possibility of a wide variation in properties. At present, these materials have found application as sealing materials [1], substrates for catalysts [2], effective sorbents of petroleum products [3, 4]. Due to the high in-plane thermal conductivity of up to 200 W/(m·K) and low density, compressed expanded graphite is actively used as heat distributors and heat sinks in various electronic devices [5]. However, through-plane thermal conductivity is quite low and varies within 3–5 W/(m·K). A common way for increasing the thermal conductivity is the producing of composite materials based on a thermal conductive additive – silver, copper. The general approach is to apply metal compounds to the substrate in various ways,

followed by annealing at high temperature and reduction of the oxides to the metal. In this way the authors of the paper [4] successfully obtained Fe-Gr composite by exfoliation of graphite intercalation compound modified with iron nitrate (III) followed by reduction treatment in hydrogen. In fact, this approach is quite energy-intensive. Therefore, determination of conditions for metal – expanded graphite composite production without additional reduction treatment is important.

During graphite intercalated compound (GIC) formation two parallel processes take place:

1) graphite matrix oxidation which leads to formation of the macrocation Cp^+ (p – number of carbon atoms of the macrocation);

2) intercalation of macroanion $A^-·mHA$ into the positively charged graphite matrix. Oxidation and intercalation effects occurs simultaneously when nitric acid is used, it makes HNO_3 distinctive from other acids [6].

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As known [6, 7] hydrolysis is a stage of traditional EG production technology, which result in GIC destruction and formation of oxidized graphite. The method of EG production can be alleviated due to the exclusion of hydrolysis and drying steps if carbamide is added to graphite/nitric acid mixture. According to the work [8], the carbamide is a reducing agent, its excess decreases NO and NO_2 emission reducing nitrogen oxides to N_2. It's known [9] that the thermal decomposition of carbamide leads to ammonia evolving. It was assumed that heat treatment of $Cu(NO_3)_2$ – containing sample would lead to copper formation because of either copper oxide decomposition (if t > 1000 °C) or its reduction by evolved ammonia.

2. Experimental

In our experiments, we used natural graphite with a carbon content of 99.8% and main fraction of 0.2 mm, 95% nitric acid (reagent grade), granular carbamide (reagent grade) with a grain size of 2 mm and $Cu(NO_3)_2 \cdot 3H_2O$ (reagent grade). Crystals of $Cu(NO_3)_2 \cdot 3H_2O$ were grinded in mortar into a powder with particles size 20–30 μm. Graphite powder was mixed with nitric acid at the mass ratio 1 : 0.4 with vigorous stirring on a mechanical stirrer for 30 min. After that $Cu(NO_3)_2 \cdot 3H_2O$ mixed with carbamide was added to graphite nitrate and stirred for 20 min in achieving free flowing substance. The carbamide ratio was the same (graphite : $(NH_4)_2CO$ = 1 : 0.8–80%) for all experimental samples while four different proportions of copper nitrate were used: graphite: from 5% – $Cu(NO_3)_2 \cdot 3H_2O$ = 1 : 0.05; to 30% – graphite : $Cu(NO_3)_2 \cdot 3H_2O$ = 1 : 0.3. Also one GIC were synthesized without copper nitrate addition according to described technique.

After the synthesis, rapid heat treatment for 2–3 sec to obtain expanded graphite based composite material were conducted in a horizontal quartz reactor at three different temperatures: 800, 1000 and 1200 °C in air atmosphere. Heat treatment at 1200 °C was conducted in nitrogen as well.

The X-ray phase analysis was performed on a THERMO ARL X´TRA diffractometer (CuK$_{\alpha1+2}$ radiation, λ = 1.5406 and 1.5443 Å, a Peltier semiconductor detector, imaging in the reflection geometry). The diffraction patterns were recorded in the 2 range of 20–60° with a step of 0.02°.

The microstructure of obtained samples was studied using VEGA3 LMU (Tescan) SUPRA 50VP scanning electron microscope.

The bulk density (g/l) was calculated according to Eq. (1):

$$d_{EG} = m_{EG}/V_{EG} \qquad (1)$$

where m_{EG} is expanded graphite mass, V_{EG} is expanded graphite volume.

Copper in the samples was determined by thermogravimetry (TG): expanded graphite powder pressed into a pellet was placed in a crucible and burned in air at 900 °C over a period of 3 h until achieving a constant weight. The CuO content was calculated using Eq. (2):

$$\omega(Cu) = m_{CuO}/m_{EG} \cdot (Mr\,(Cu))/(Mr\,(CuO)) \cdot 100\% \quad (2)$$

where m_{EG} – is a mass of copper modified expanded graphite, $Mr(Cu)$ and $Mr(CuO)$ – molar mass of copper and copper (II) oxide respectively.

The heat capacity of the specimens was determined within the range from -50 to 100 °C by differential scanning calorimetry (DSC) performed on calorimeter DSC 204 Phoenix (Netzsch). A sapphire disk was used as the standard. The mass of the specimen was chosen so that the DSC signal of the specimen and the standard would differ by no more than 30%. The thermal diffusivity of the high-temperature expanded graphite-based materials within the range from 30 to 900 °C was evaluated by the laser flash method on thermal analyzer LFA 457 MicroFlash (Netzsch). The calculation was performed using a mathematical model that accounts for radiative heat losses. Thermal conductivity, W/(m·K), was calculated with the use of the specimens' specific heat and apparent density in accordance with the formulas:

$$l = ac_p\,\rho \times 10^{-3} \qquad (3)$$

where a is thermal diffusivity, mm^2/sec; c_p is specific heat, J/(g·K); ρ is the apparent density of the specimen, kg/m^3.

3. Results and discussion

According to literature data [10] hydrated copper nitrate is converted to copper (II) oxide at 263 · 310 °C:

$$2Cu(NO_3)_2 \cdot 3H_2O \xrightarrow{t} 2CuO + 4NO_2 + 6H_2O + O_2$$
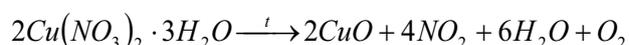
It was determined by X-ray phase analysis that obtained samples of EG-based composites contain

three different phases of copper compounds: Cu, Cu_2O and CuO. A ratio of copper and its oxides depends on preparation conditions. If GIC is heat treated at 1000 or 1200 °C the main phases are Cu and Cu_2O, and a peak with the highest intensity on a diagram (Fig. 1b, c) corresponds to copper. As known [11], copper (II) oxide decomposes at 1026 °C.

Since copper (II) oxide is stable at 800 °C, it was supposed that heat treatment temperature reduction should have increased CuO ratio in composite material. According to X-ray phase analysis of samples obtained at 800 °C peaks with high intensity correspond to copper (I), (II) oxides (Fig. 1a). Cu_2O formation could be explained by reduction with ammonia, which reduces CuO to Cu_2O and Cu in the range of 425–700 °C [12]. The increasing of local thermolysis temperature connected with carbamide decomposition can be another factor of copper (I) oxide formation. The same reasons are presumable accounted for the presence of copper in samples prepared at 1000 °C.

Thermal expansion in nitrogen allows to exclude the oxidation of copper in the air, and as a result, increase the content of Cu in graphite material. This conclusion is confirmed by changing intensity ratio of Cu, Cu_2O and CuO peaks. It was determined by X-ray phase analysis that samples heat treated in nitrogen at 1200 °C contain Cu phase without significant amount of copper oxides (Fig. 1d). Thus the formation and ratio of copper phases (Cu, Cu_2O and CuO) is controlled by the process parameters: exfoliation temperature and
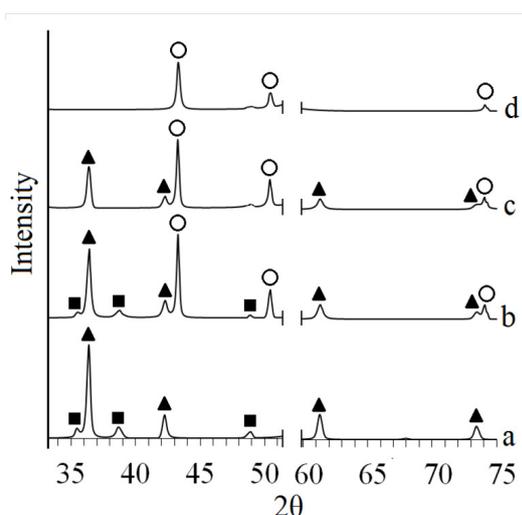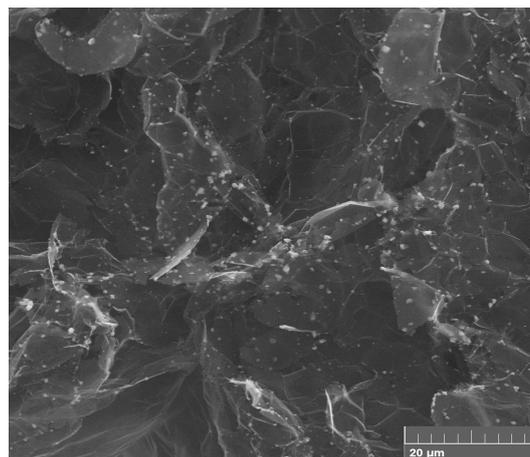

Fig. 2. SEM images of exfoliated graphite sample prepared with addition 10% $Cu(NO_3)_2$.

atmosphere. In order to obtain Cu/graphite composite GIC mixed with copper nitrate and carbamide was heat treated in nitrogen at 1200 °C. The further samples characterization relates to these preparation conditions.

According to thermogravimetric analysis data the average content of copper in EG samples prepared with 10% $Cu(NO_3)_2$ mixture is 3%. The $Cu(NO_3)_2$ ratio increase up to 30% result in the copper content growth up to 8%.

SEM images of EG samples are shown on Fig. 2. Solid-phase copper containing particles are distributed non-uniformly on graphite surface, it seems that the distribution character is caused by copper nitrate adsorption on defects of graphite matrix and on the edges of graphite crystallites. The average particles size is below 2 μm. Bulk density of obtained samples is comparatively low, it varies from 1 to 2 g/l. So the proposed technique allows to keep high exfoliation degree for even if nitric acid and then $Cu(NO_3)_2 \cdot 3H_2O$ is added without further drying.

The thermal conductivity of copper-graphite composites was discussed in [13–19]. It's known from works [13, 14], where TC of materials prepared from the mixture of copper and graphite powder by the powder metallurgy method was measured, that the rise of volume copper fraction leads to drastic thermal conductivity growth for >50% vol% Cu content. According to [15] the TC achieved in the composites depends on the graphite type used, the heat treatment during consolidation and the volume fraction of graphite. The density of obtained metal-graphite composite Cu-graphite composites [13] varied from 6.1 to 8.9 g/cm^3 which is not suitable for thermal management applications where the weight of material is crucial.

Fig. 1. X-ray phase analysis diagram of EG sample prepared with addition 10% $Cu(NO_3)_2$. The samples were heat treated at: (a) 800 °C in air; (b) 1000 °C in air; (c) 1200 °C in air; (d) 1200 °C in nitrogen. The peaks have been assigned to Cu (○), Cu_2O (▲), CuO (■).

Table
The influence of copper content in EG samples on thermal conductivity

$Cu(NO_3)_2 \cdot 3H_2O$ ratio, %	Cu content in EG samples, %	Thermal conductivity, W/(m·K)	Specific heat capacitiy, J/(g·K)
0	0	4.9	0.73
5	2.1	5.7	0.73
10	2.9	6.0	0.72
20	4.8	5.3	0.66
30	8.2	4.5	0.62

In order to decrease the density of copper-graphite composite the Cu content reduction is required. According to interpolation [13] of Kováčik's data the composite TC in 0–20 vol.% Cu range is almost constant and close to graphite TC. In present work the possibility of enhancing the thermal conductivity of expanded graphite via doping by copper in a 0–8% range was demonstrated. The dependence of copper graphite composite TC from Cu content has non-linear character (Table).

Doping EG with up to 3% Cu leads to thermal conductivity increase by up to 20% while further copper content growth up to 8% cause a TC drop. The thermal conductivity of graphite composite doped with 8% Cu is even lower than for graphite.

The non-linear character of TC dependence from copper content seems to be primary caused by specific heat capacity reduction in 3–8% Cu range from 0.72 to 0.62 J/(g·K) (Table). According to Eq. 3 thermal conductivity is in direct ratio to specific heat capacity and thermal diffusivity. The doping of expanded graphite by <3% copper leads to thermal diffusivity growth without significant impact on specific heat capacity. The further copper content increase up to 8% results in specific heat capacity reduction from 0.72 to 0.62 J/(g·K) which is not accompanied by thermal diffusivity growth and cause a TC drop.

4. Conclusions

Thus, it has been shown that the composition of expanded graphite – Cu composite materials strongly depends on the temperature and the atmosphere of thermal expansion. The proposed experimental technique based on exfoliation of intercalated graphite and copper compounds in nitrogen at 1200 °C allowed to produce expanded graphite-based composite material containing Cu phase without significant amount of copper oxides. The dependence of copper graphite composite TC from Cu content has non-linear character with maximum value of 6.0 W/(m·K) at Cu content of 3%. The modification of expanded graphite by copper doesn't require to complicate EG production technique. Moreover, GIC hydrolysis and drying steps are excluded by virtue of carbamide addition.

Acknowledgements

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