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Copper-based Composite Materials Reinforced with Carbon Nanostructures

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The present work is devoted to development of high performance Cu-based material reinforced with carbon. For this purpose Cu-C composite powders were produced by one-step CVD process. The powders containing carbon nanofibers and graphene were subjected to compacting and analyzed. Mechanical properties of Cu-carbon nanofibers (CNFs) and Cu-graphene composites were compared to traditional Cu-graphite and pure copper samples compacted under the same technology. Cu-CNFs material showed the best performance (1.7 times increase in the hardness compared to copper), that is primarily explained by the smallest matrix grain size, which growth is inhibited by the homogeneously dispersed CNFs. Friction coefficient of the Cu-(17 – 33) vol.%CNF was found to be 9 times less than that of pure copper and coincides within the error with Cu-graphite, however the wear of Cu-33 vol.%CNF reduced by more than 2 times over Cu-33 vol.% graphite samples.

Keywords: copper-based composite, carbon nanostructures, chemical vapor deposition, mechanical properties, wear.

1. INTRODUCTION

Owing to their great physic-mechanical properties carbon nanostructures are especially important as reinforcing component in metal-based composites, even though a little amount of carbon nanotubes (CNTs) or carbon nanofibers (CNFs) is capable to enhance mechanical and electrical properties [1]. Among them copper is one of the most industrially important metals, which for many applications requires improvement in mechanical strength [2]. Copper-graphite composites are widely known as material for sliding electrical contacts, due to high thermal and electrical conductivities closed to pure copper and low friction coefficient caused by graphite lubricating ability [3 – 8]. At the same time in the recent decade a number of studies have been devoted to copper-based composites reinforced with carbon nanostructures – nanotubes (CNTs) or fibers (CNFs) [9 – 19]. It is well known, that the homogeneity of the reinforcing components distribution along with good interfacial bonding are key points for improvement of the mechanical and tribological properties [1]. To meet these demands the carbon nanostructures were coated with Ni [9, 10] or Cu [11]; in [13] multistep molecular-level-mixing process was proposed resulting in a 76.9 % decrease in wear loss. Application of copper particles as a catalyst for carbon nanostructures growth was as well considered. For example, synthesis of octopus-like carbon nanostructures on copper nanoparticles has been recently reported in [20], however, this method shows relatively low effect on the mechanical properties.

The aim of this work was to investigate the possibility to produce high performance Cu-based material modified with carbon nanostructures by means of chemical vapor deposition method, to analyze the mechanical and tribological properties of the composites.

2. EXPERIMENTAL DETAILS

The synthesis of CNFs on the surface of copper powder was carried out in a simple one-step CVD process. For the synthesis we used the experimental setup described in [21, 22]. It consisted of a quartz tube heated in a resistive furnace in the temperature range from 700 to 940 °C. Copper metal powder of 99 % purity that has an average particle size of 2 – 5 µm was used as the matrix. For the synthesis of carbon nanomaterials, the reactor was heated to the synthesis temperature in an Ar atmosphere. After 5 min, Ar was replaced by H_2 for 5 min reduction. The growth of CNFs was conducted in acetylene – hydrogen and ethylene – hydrogen atmosphere with a various C:H. After 20 min, the acetylene – hydrogen gas mixture was replaced by Ar and the crucible was cooled down to room temperature. In order to fabricate the compact composites of preassigned composition the produced powders were mechanically mixed with a certain amount of pure copper powder. The prepared powders were consolidated by traditional powder metallurgy routine. The powder mixtures were cold pressed at 500 – 600 MPa using a cylindrical mold of a diameter 8 mm. The sintering was carried out at 950 °C during 2 h in an H_2 atmosphere. For comparison pure Cu and Cu-graphite powders were consolidated under the same conditions. Some of the synthesized samples were subjected to cold rolling in a laboratory double roller mill with the roll diameter of 90 mm and rolling speed of 0.3 m/sec. Rolling was carried out in two stages with intermediate 900 °C annealing the sample during for 1 hour in a hydrogen atmosphere. The total volume reduction was achieved to be 70 %. The final annealing was carried out at 420 °C also for one hour in a hydrogen atmosphere.

Microscopic investigations of the produced materials were carried out with the help of a high resolution analytical scanning electron microscope (SEM) equipped with field emission gun FE-SEM JEOL 7500FA and high

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resolution transmission electron microscope (TEM) JEOL JEM2200FS with corrector of spherical aberrations (Cs ≤ 0.005 mm). For TEM observation, the samples were dispersed and treated in ethanol by tip ultrasonicator (Branson 450D, microtip) at the power of 40 W (3 × 3 second pulses).

Brinell hardness was measured by a hardness tester Zwick/Roell ZHU by using 2.5 mm steel ball at the load of 62.5 kg. Elongation measurements of the sample were carried out using a tensile machine IR-5040-5 with a maximum load of 5 kN applying a three-point bending procedure. Samples for the test were prepared in the form of a plate with the size of $20 \times 5 \times 1\ mm^3$. The friction tests were conducted on an end tribometer using a pin-on-disc scheme. The counter material was a copper (C11000) ring. Sliding was performed under dry friction at ambient conditions (room temperature 24 °C and humidity 50 %); linear velocity and constant load were set up as 0.8 m/s and 20 N correspondingly. Before each test the samples and counterpart surfaces were cleaned and polished. The wear (I) was calculated out from the loss of each specimen's volume and way of friction according to: $I = V/SL$, where V is the volume loss, S is the contact area, L is the track length. The coefficients of the friction were obtained by measuring the tangential force on the specimen using a strain gauge bridge.

3. RESULTS AND DISCUSSION

Fig. 1 shows some typical temperature dependences of the powder weight yield earned at varying experiment conditions: gas content and substrate particles morphology. As can be seen all the dependencies have maximums, positions of which are determined by gas content. The carbon deposit yield at temperature left of the maximum is mainly controlled by hydrocarbon precursor decomposition on the metal substrate surface; however, at temperatures right of the maximum the regime changes to an adsorption-controlled one: hydrocarbon decomposes with a formation of aerosol carbon particles [23], which is deposited on the cold parts of the reactor. Utilizing dendritic particles resulted in very insignificantly higher weight yield compared to round shape ones, obviously owing to higher substrate specific surface.

As revealed by SEM observation, independently on the gas precursor, carbon product synthesized at temperature interval left of the maximums was amorphous. SEM images of the copper powder treated at temperatures of 740 and 940 °C in acetylene and ethylene atmosphere correspondingly are presented in Fig. 2. As seen from the picture the specimens treated in acetylene revealed abundance of high aspect ratio nanofibers (Fig. 2 a), however the particles treated in ethylene don't revealed any fibers, but are covered by a smooth carbon layer.

TEM images of the carbon coatings removed from the copper particles treated in ethylene are presented on inset of Fig. 2 b. As it was observed by TEM the carbon coatings obtained at temperature of 940 °C contained 8 – 12 layers of graphene with interplanar distance of 0.373 ± 0.05 nm. At lower temperatures only amorphous carbon was found. In an attempt to decrease the number of the layers, the duration of the treatment was decreased from 20 to 10 min. However, neither the weight of the sample, nor the number of the layers changed with shorter growth time. Therefore, for the mechanical tests we utilized the samples prepared at 10 min growth time.

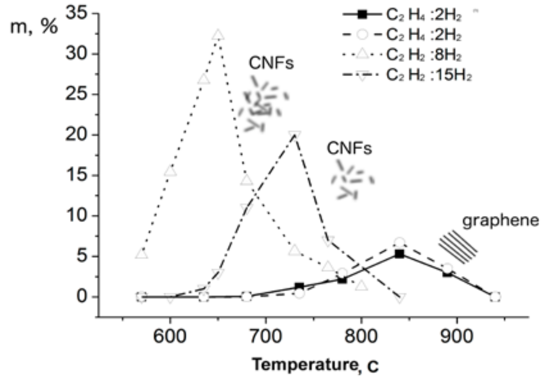


Fig. 1. Temperature dependence of the sample weight after 20 min treatment in different carbon sources, using dendritic (circles) and spherical substrate particles (others)

Thus, the Cu-C composite powders containing either CNFs or graphene layers were synthesized. To evaluate their properties the Cu-CNFs powders were compacted through cold isostatic pressing with subsequent sintering. However, the syntheses of the graphene proceeds at temperatures about 940 °C, when significant sintering of the copper powder occurs, that makes impossible to apply the same technological route, so the partly sintered Cu-graphene powders were subjected to cold rolling.

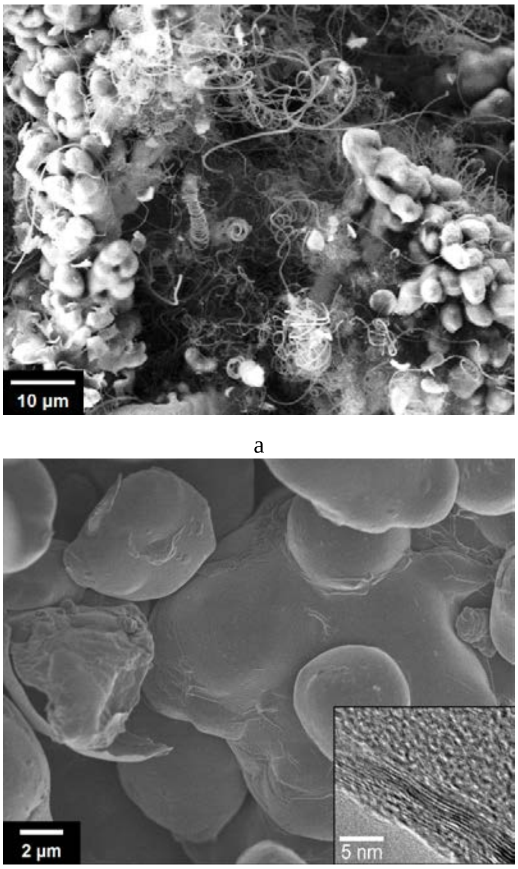


Fig. 2. The copper powder treated in acetylene at temperature of 740 °C (a) and in ethylene at temperature of 940 °C (b)

The results of the mechanical tests of Cu-9 vol. %C composites are presented in Table 1. As expected, any carbon additions to copper led to hardening of the composite and a decrease in the ductility compared to pure copper. The best results were obtained for Cu-CNFs composite, this material showed 1.7 times increase in the hardness compared to pure copper. Copper hardened by graphene showed only 39 % increase in HB with significant ductility decrease.

Table 1. Mechanical properties of Cu-9 vol. %C composites

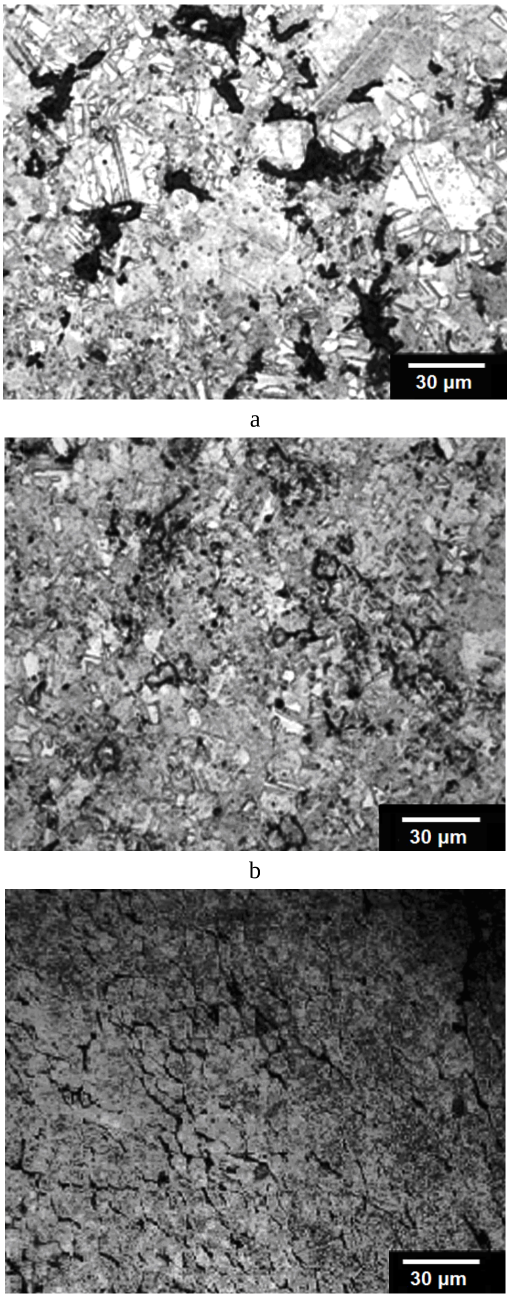
Material	HB	δ, %
Cu	35	55
Cu-9 vol.%graphite	38	19
Cu-9 vol.%CNFs	60	38
Cu-9 vol.%graphene	48	19

For understanding the reason of the mechanical properties change the microstructures of the sintered samples were analyzed, their images are presented in Fig. 3. As can be seen from Fig. 3 a, the microstructure of Cu-graphite composite consists of 10 μm – sized matrix grains (similar to pure copper sample) and very rough carbon inclusions. Cu-CNF composite contains finer grains (around 4 μm) with carbon homogeneously dispersed between them (Fig. 3 b). Apparently a good dispersion of CNFs in the matrix prevented the grain growth during sintering. In case of Cu-graphene there were observed the grains of size 6 – 8 μm elongated in the rolling direction with fine carbon layers located between (Fig. 3 c). The plastic deformation of the copper particles during rolling resulted in a disruption of less plastic graphene layers attached to the particles surfaces; therefore, graphene only partially blocked growth of the Cu grains.

Cu-CNFs composite has the narrowest grain size distribution with the maximum corresponding to 4 μm. Therefore, the best mechanical properties of the Cu-CNFs composite can be explained by the smallest Cu grain size. To confirm primary influence of the grain size refinement on the material hardness, the Hall-Petch relationship was built, it is presented on Fig. 4. As one can see, independently on the carbon morphology the copper grain size is determinant for the composite hardness and CNFs has the most pronounced refinement effect.

Thus, from the practical point of view carbon nanofibers grown on the surface of copper particles are the most preferable: first of all, CNFs synthesis requires lower temperature and cheaper carbon source (acetylene); and the second, the produced composite has smaller grain size resulting in the best properties.

Fig. 5 demonstrates HB of Cu-CNFs composites depending on the carbon content. Reinforcement of copper by CNFs has a maximum at 9 vol. % CNFs, similar behavior was observed in [9, 10]. The decrease in hardness at higher carbon content may be explained by thickening of the grain boundary CNFs clusters while retaining the same matrix grain size [24].



a

b

c

Fig. 3. Microstructures of the composite materials: a – Cu-9 vol.% graphite; b – Cu-9 vol.%CNFs; c – Cu-9 vol.% graphene

As known Cu-graphite composites are of great interest from the point of tribological application, so the tribological characteristics of the proposed Cu-CNFs material were investigated and compared to traditional Cu-graphite ones. The composition 17-33 vol.% of carbon was chosen basing on industrial Cu-graphite composite (Russian Standard - GOST 26719-85).

Coefficient of friction and wear loss of the tested materials are presented in Table 2. Wear in Cu-33 vol. %CNFs material reduced by more than 8 times compared to pure copper and by 2 times over Cu-33 vol.% graphite samples.

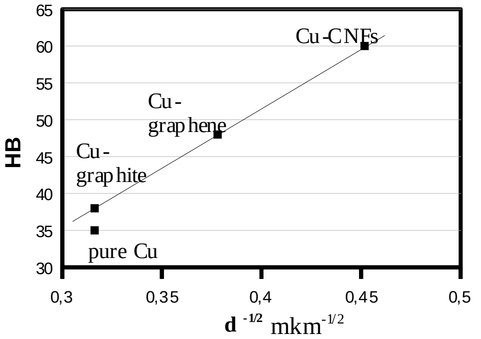


Fig. 4. Hall-Petch relationship for Cu-9 vol. %C

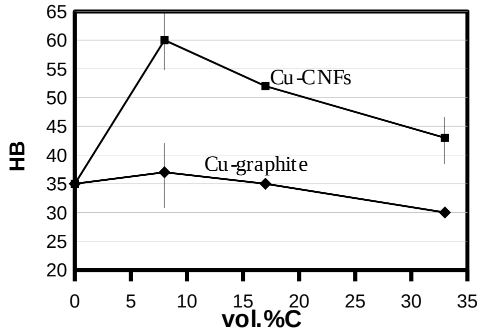


Fig. 5. Hardness of Cu-C composite materials [21]

Images of the friction surfaces are presented on the Fig. 6. As reported in [5, 8] the prevail wear mechanisms of Cu-graphite composite under similar load is delamination: shear stress occurred under counterparts sliding causes nucleation and growth of the cracks in subsurface area resulting in detachment of the upper layers [8]. Under copper plastic deformation graphite particles squeeze out and smear over contact surface, this graphite debris impede adhesive wear and decrease of friction coefficient by reducing metal to metal contact points (Fig. 6 a).

Table 2. Tribological properties of Cu-C composites

Material	Coefficient of Friction	Wear, $\times 10^{-6}$
Cu	0.9	22.0
Cu-33 vol.%graphite	0.16	6.0
Cu-17 vol.%CNFs	0.13	6.2
Cu-33 vol.%CNFs	0.08	2.5

It is clearly seen from the worn surface image (Fig. 6 b), that the wear of the Cu-CNFs composites occurs through thin flakes exfoliation what is a characteristics of delamination wear as well. Considering the higher hardness of Cu-CNFs composite over Cu-graphite one (Fig. 5), plastic deformation of the copper matrix affects thinner subsurface area. Due to composite powder preparation method applied in this work, the copper grains are covered by CNFs layer, and, as was mentioned above, the copper matrix itself has finer grain structure, so the cracks caused by shear stress propagate along this CNFs reach boundary layer in the very upper subsurface area (Fig. 6 c), resulting in the fine flakes exfoliation.

Thus, the reduction of the friction coefficient observed in this material is caused in less degree by the lubricating effect of the squeezed out carbon debris, but mainly by the disruption and sliding very thin flakes along grain boundaries enriched with CNFs. So the exfoliation of the thinner layers compared to Cu-graphite composite explains the reduction of the wear loss observed in Cu-33 vol. %CNFs.

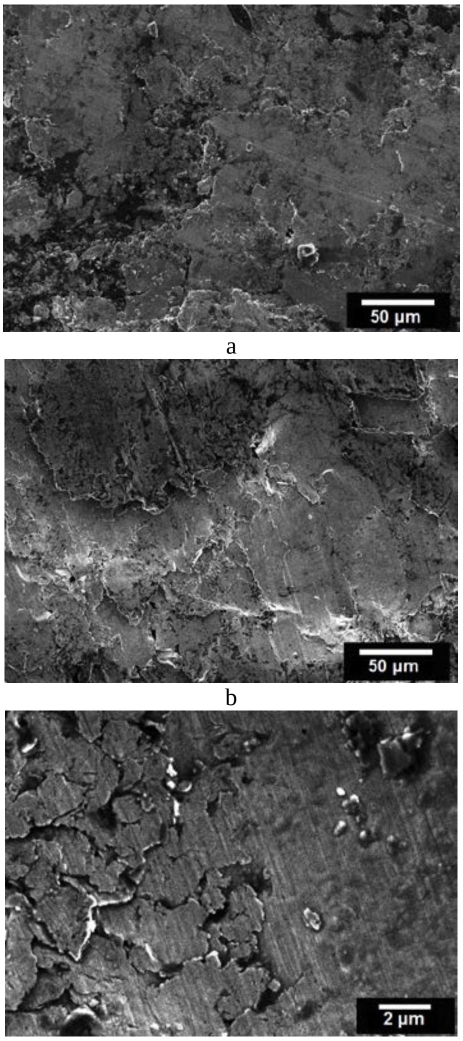


Fig. 6. SEM images of the friction surfaces of the Cu-33vol.% graphite (a) and Cu-33vol.%CNFs (b,c)

4. CONCLUSIONS

Cu-CNF, Cu-graphene composite materials were synthesized by one-step CVD process with subsequent compacting. Comparative analysis of their mechanical properties referred to pure copper and traditional Cu-graphite composites was performed. Cu-CNFs material showed 1.7 times increase in the hardness compared to pure copper. Copper hardened by graphene showed only 39 % increase in HB with significant ductility decrease. The best mechanical properties of the Cu-CNFs composite is primarily explained by the smallest Cu grain size, which growth is inhibited by the homogeneously dispersed CNFs. The tribological properties of Cu-CNFs samples were evaluated in comparison to well known Cu-graphite composite materials consolidated by the same technology. Friction coefficient of the Cu-(17-33) vol.%CNF is 9 times less than that of pure copper and coincides within the error with Cu-graphite composites. However, the reduction of the friction coefficient observed in this material is in less degree caused by squeezed out lubricating carbon debris, but mainly due to the disruption and sliding very thin flakes along intergranular CNFs clusters. Due to this mechanism the wear in Cu-33 vol. %CNFs material reduced by more than 2 times over Cu-33 vol. % graphite samples.

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