Properties of the Cu-graphene composites produced by high pressure torsion

Właściwości kompozytów Cu-grafen wytworzonych skręcaniem pod wysokim ciśnieniem

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The investigations concerning Cu-graphene composites produced by powders consolidation with direct use of high pressure torsion (HPT) are presented. The HPT parameters were determined. The XRD and transmission electron microscopy revealed very refined matrix and graphene sheets microstructures. The Raman spectroscopy confirmed dispersed state of the graphene with a large defects concentration.
KEYWORDS: graphene, copper-matrix composite, high pressure torsion

Zaprezentowano wyniki badań dotyczące wytwarzania i właściwości kompozytów Cu-grafen metodą skręcania pod wysokim ciśnieniem (HPT). Określono parametry konsolidacji. Metodami dyfrakcji rentgenowskiej i transmisyjnej mikroskopii elektronowej pokazano bardzo rozdrobnioną strukturę matrycy i warstw grafenowych. Bardzo rozdrobnioną strukturę, jak i dużą koncentrację defektów w grafenie potwierdziła także spektroskopia Ramana.
SŁOWA KLUCZOWE: grafen, kompozyt miedź-grafen, skręcanie pod wysokim ciśnieniem

Graphene (GN), as a pure 2D material revealed extraordinary mechanical, thermal and transport properties [1] evoking great expectations in materials science, concerning potential improvement in properties of materials. One of the subjects is the improvement of metal matrix composites [2]. In fact, such improvement was first achieved for the polymer-matrix composites [2]. Recently, many impressing results concerning metal matrix composites were presented in literature [3].

The methods of severe plastic deformation (SPD) were originally invented for the refinement of the metallic materials structures [4]. Between them, high pressure torsion (HPT) revealed increasing range of application from the pure metallic materials structure refinement, through ceramic materials to amorphous powders consolidation [5]. The idea of the investigations was to apply HPT method supported by the mechanical alloying (MA) for the synthesis of the composite structure of Cu matrix with graphene addition. Such composite could be applied as a heat-sink material for the effective cooling of the electronic devices. The results of similar investigations concerning Al-graphene and Al-graphene oxide composites were presented previously [6].

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The method of the composites preparation

The samples were prepared directly from the copper and graphene powders. The preliminary step of mechanical alloying, used in the case of Al-graphene composites preparation [6] was omitted, to decrease possible oxidation of the Cu powder. The powder was of 99.99 purity, round shaped, about 1 mm in diameter. The graphene from Angston Materials, (N0006-010-P batch 032613-05R-B) was used. In comparison with Al-graphene composites [6] the amount of graphene was increased to 2% vol. The powders, well mixed, were further consolidated in HPT equipment built on the base of the hydraulic press DE-2430-01 with the fully control rotation system. The special type of the constrained anvils was used for the powders mixture consolidation. For comparison, also samples from Cu – 2% vol. graphene oxide (GO) mixture and from seldom Cu powder were produced in the same way. The parameters of the process were chosen on the base of experience gained in the Al-graphene composites production [6] consisting on hydrostatic pressure 4 GPa and as much as 10 rotations.

The questions concerns both differences in ability for consolidation of powders due to intensive deformation and the range of deformation required for the fully unified structure of the Cu matrix composites. To answer the first question the parameter of the relative compression C was calculated along radii of the samples assuming lack of compression at the centre:

$$C(r) = (D(r)\text{-}D_0)/D_0 \quad (1)$$

where: D – thickness at r and D_0 – thickness in the centre of the sample.

For the Cu-GN composites $C(r)$ increased from 0.0 at the center to -0.653 at the very edge of the samples. The comparison with the Cu-GO and compressed Cu samples revealed that graphene addition clearly increased ability for the compression at radii r above 0.5 mm.
The generally accepted formula for the effective deformation by the HPT does not exist. In the paper two following formulas are used [7]:

$$\gamma = 2\pi N(r / D(r)) \quad (2)$$

where: γ – shear strain, N – number of rotations

and

$$\varepsilon = (2/3)^{1/3} \ln[(1+\gamma^2/4 + \gamma/2)^{1/2}] \quad (3)$$

where ε means equivalent strain.

The comparison of ε versus r for the different consolidated samples is shown in Fig. 1. As is visible, the Cu-GN sample reveals larger value of ε at each r value, than Cu and Cu-GO samples, increasing from 500 to 700%. The observed highest ability of Cu-GN composites for compression and deformation may result of the known lubricating ability of GN.

The structure of the composites

The XRD did not supply any information concerning graphene or graphene oxide in spite of the relatively large content of 2% vol. The Williamson-Hall plot made possible to determine for all the samples the average size of the Scherer's domains of coherent diffraction as well as the deformation of the lattice. The results are given in the table.

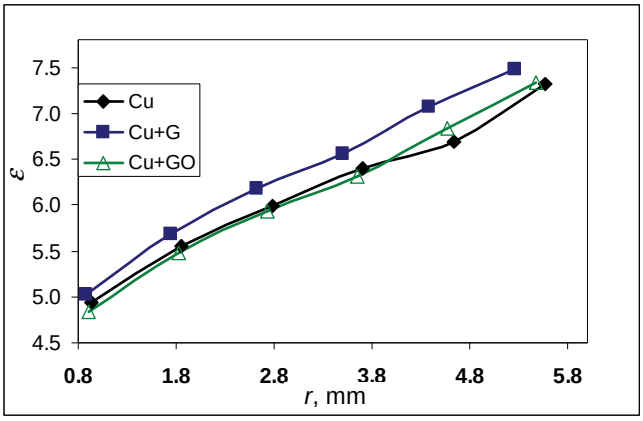

Fig. 1. The comparison of the equivalent strains versus radii calculated for all the samples with the equations (2) and (3)

TABLE. Size of the Scherer's domains of coherent diffraction and the deformation of the lattice of Cu

Sample	Coherent domains size, nm	Lattice deformation, %
Cu	54.9	0.5
Cu-2%vol.GN	55.5	0.6
Cu-2%vol.GO	25.0	0.5

As may be noticed the sizes of the domains, which may be identified with the grains of the Cu matrix, are similar in case of the Cu sample and Cu-GN composite, while are half of that for the Cu-GO composite. As results, the graphene has no influence of the grains fragmentation in the consolidation process but the graphene oxide does. The lattice deformation in all the samples remains similar.

The large fragmentation of the Cu-GN structure is also visible in Fig. 2 presenting microstructure in the transmission electron microscopy (TEM) resolution. Small grains of the matrix, in the range of 50 nm are visible in the bright field (BF) and dark field technique (DF) (Fig. 2*a*, *c*). Also ring-type electron diffraction pattern (SADP) is very characteristic for the extremely small grained, statistically oriented crystalline structure (Fig. 2*b*).

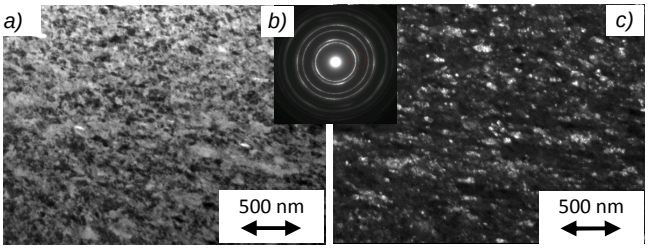

Fig. 2. TEM microstructure of the Cu-GN sample *a*) BF, *b*) SADP, *c*) DF

The average grain size estimated from the TEM microstructure remains in agreement with the size of the coherent domains presented in the table.

The graphene sheets are not visible in Fig. 2, however large magnification together with the slight defocusing enables to identify graphene in the form of small particles on the surface of the matrix grains (Fig. 3). The picture confirms strong dispersion of the graphene, very different in comparison with the graphene sheets observed in the case of Al-GN composites [6].

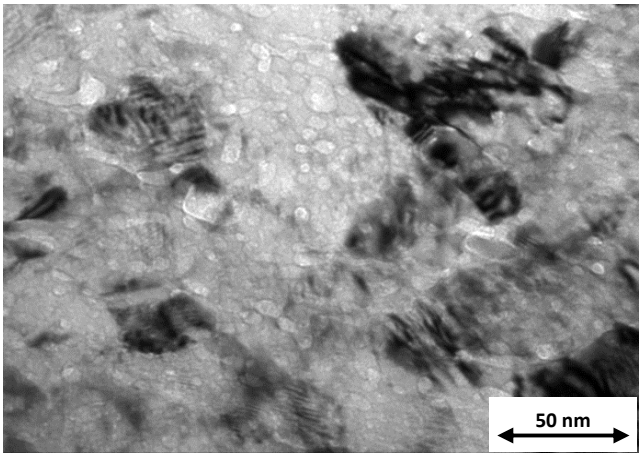

Fig. 3. TEM microstructure of the Cu-GN composite, BF, slightly defocused

Conclusions

The method of constrained high pressure torsion was successfully used for the consolidation of Cu-graphene and Cu-graphene oxide powders giving homogenous structure of composites.

Graphene addition increases ability of metal powder to consolidate as well as increases attainable equivalent strain.

The microstructure of the Cu-graphene composites prepared with 4 GPa hydrostatic pressure and 10 rotations of the anvils consisted of the highly fragmented Cu matrix grains, in the range of 50 nm size and very dispersed graphene particles.

In comparison with pure Cu powder the graphene addition did not influenced fragmentation of the Cu powders during the HPT processing of the composite.

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