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COMPOSITES THEORY AND PRACTICE

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SILVER MATRIX COMPOSITES CONSOLIDATED AND HOT EXTRUDED FROM BALL MILLED POWDERS STRENGTHENED WITH DIFFERENT TYPES OF GRAPHENE PLATELETS

Silver matrix composites containing 1÷2% graphene platelets of various thicknesses were uniaxially hot pressed at 480°C in vacuum from powders ball milled for 5 hours. Two kinds of graphene nanoplatelets were added: (i) - nanoflakes (FLRGO) of a thickness 2÷4 nm, which led to a higher hardness (35÷49 HV) and slightly lower electrical resistivity of the composites, than that of pure hot pressed Ag and (ii) - nanographite platelets (N006) 10÷20 nm thick as confirmed by electron microscopy, which caused a similar increase in hardness up to 34÷45 HV and about a 40% higher electrical resistivity than that of pure hot pressed Ag. SEM studies showed a more homogeneous microstructure of the composites with the FLRGO graphene additions. TEM studies confirmed refinement of the thickness and lateral size of the graphene particles after milling and hot compaction down to a few nm manifested by diffused electron diffraction. The hot extrusion of hot pressed composites with FLRGO platelets caused the growth of graphene platelets and coagulation of the platelets, which contributed to a higher hardness and electrical resistivity.

Keywords: metal matrix composites, graphene platelets, electron microscopy, ball milling, powder metallurgy

KOMPOZYTY NA OSNOWIE SREBRA PRASOWANE I WYCISKANE NA GORĄCO Z MIELONYCH PROSZKÓW UMACNIANYCH PŁYTKAMI GRAFENOWYMI O RÓŻNEJ WIELKOŚCI

Kompozyty na osnowie srebra z dodatkiem płytek grafenowych o różnej grubości zostały wykonane poprzez jednoosiowe prasowanie w temperaturze 480°C z proszków mielonych 5 godzin w młynkach kulowych. Zastosowano dwa rodzaje płytek grafenowych: (i) nanopłatki FLRGO z firmy Nanomaterials o grubości 2÷4 nm, które powodowały wzrost twardości kompozytów na osnowie srebra, do wielkości 35÷49 HV i nieznaczny spadek oporności w stosunku do czystego prasowanego z proszku srebra oraz (ii) płytki nanografitu N006, których dodatek w ilości 2% wag. potwierdzono za pomocą dyfrakcji rentgenowskiej i elektronowej z firmy Angstron Materials o grubości płytek 10÷20 nm, powodował wzrost twardości do 34÷45 HV i oporności elektrycznej o około 40% w stosunku do czystego prasowanego z proszku srebra. Badania mikrostruktury metodami SEM wykazały występowanie bardziej jednorodnej mikrostruktury w kompozytach zawierających płytki grafenowe FLRGO. Badania TEM wykazały rozdrobnienie płytek N006 po mieleniu i prasowaniu, co powodowało silne rozmycie refleksów 002 grafenu w związku ze zmniejszeniem wielkości cząstek w płytkach do kilku nm. Prasowanie na gorąco spowodowało z kolei wzrost wielkości cząstek w płytkach i koagulację płytek, co wpłynęło na wzrost twardości i oporności elektrycznej.

Słowa kluczowe: kompozyty na osnowie metali, płytki grafenowe, mikroskopia elektronowa, mielenie kulowe, metalurgia proszków

INTRODUCTION

Graphene is a new material that has attracted significant attention as a composite component due to its unusual physical and mechanical properties such as high thermal conductivity [1] and the highest mechanical strength measured to date [2]. Silver - carbonous material composites were developed using additions of CNT (carbon nanotubes) or graphene [3-6]. The addition of CNT effectively improved the electrical conductivity and mechanical properties. Many studies have been devoted to the fabrication of metal nanoparticle-decorated CNT for their unique electrical, magnetic and optical properties [3, 4]. Ag decorated CNT were employed as conducting filler in epoxy resin to fabricate electrically conducting polymer composites showing the electrical conductivity of composites containing 0.10 wt.% Ag within CNT more than four orders of magnitude higher than those containing the same content of pristine CNT [4]. Recently, it was reported that the electrical conductance of a single graphene layer could be significantly improved by introducing highly conductive nanomaterials such as silver or copper nanowires [5]. Graphene-Ag composite films were fabricated using an easy chemical reduction method [6] and it was found there that the conductivity of the resul-

tant films can be improved via uniform decoration with Ag particles. Silver nanocrystals were used to prevent the stacking of exfoliated graphene and to improve its conductivity [7]. They were deposited onto chemically-exfoliated graphene through self-assembly and subsequent reduction of silver ions. The electrical conductivity of silver-deposited graphene increased by nearly 3 times when Ag nanoparticle/graphene hybrids were used as an electrode and the resultant current density increased significantly compared with that of an as-produced graphene electrode. Graphene nanoplatelets (graphite thin sheets with the size of less than 100 nm) exhibited extraordinary mechanical, electrical, and thermal properties [8] and showed much better strengthening efficiency than CNT and other ceramic additions in magnesium and aluminum alloy matrix bulk composites as reported in [9]. Preliminary studies of copper matrix composites strengthened with graphene platelets [10] indicated significant strengthening and a small drop in electrical conductivity, particularly when using fine graphene platelets. Therefore in the present paper, silver matrix composites were studied due to their advantageous interaction with graphene as indicated in [7]. They were strengthened with two types of graphene platelets, coarser and finer ones, to find the effect of variable graphene additions on the electrical conductivity, hardness and microstructure of bulk composites, interesting also for the improved tribological properties of graphene [11].

EXPERIMENTAL PROCEDURE

Materials

The composites were produced by uniaxial hot pressing in 10^{-2} bar vacuum at the pressure of 480 MPa and temperature of 490°C. The temperature was chosen so as to minimize the porosity and to prevent the growth of platelets. The silver powder of the particle size 40÷90 μm and purity 99.99 was supplied by Innovator SA Gliwice Poland. Two grades of graphene platelets were used. The first kind of graphene nanoplatelets type N006 used in this study was obtained from Angstron Materials. The graphene nanoplatelets have, according to the supplier, an estimated thickness of 10÷20 nm as shown in Figure 1a and the electron diffraction pattern in the corner of Figure 1a shows the interplanar distance close to that of graphite as marked in Figure 1a.

The graphene platelets from Nanomaterials LS marked FLRGO were produced by the reduction of graphene oxide with an estimated platelet thickness of 2÷4 nm and a lateral size under 100 nm. The addition of oxygen was reported to be lower than 10% and hydrogen lower than 1%. Detailed characterization of the structure of both types of graphene using HRTEM and Raman spectroscopy was given in [10]. Raman spectroscopy confirmed a much higher fraction of a few platelet layer thickness and much finer lateral size in the 002 plane of the FLRGO graphene particles as compared with N006 graphene. However, more detailed TEM studies were performed to characterize particularly the lateral size of the graphene platelets in both kinds of graphene. Figure 2 shows an image of the 002 graphene planes within the platelet showing a curved band of thickness near 4 nm consisting of fragments 3÷7 nm in length with slight misorientation and often with an amorphous structure between the crystalline fragments. It confirms the Raman spectroscopy results of FLRGO graphene platelets presented in [10].

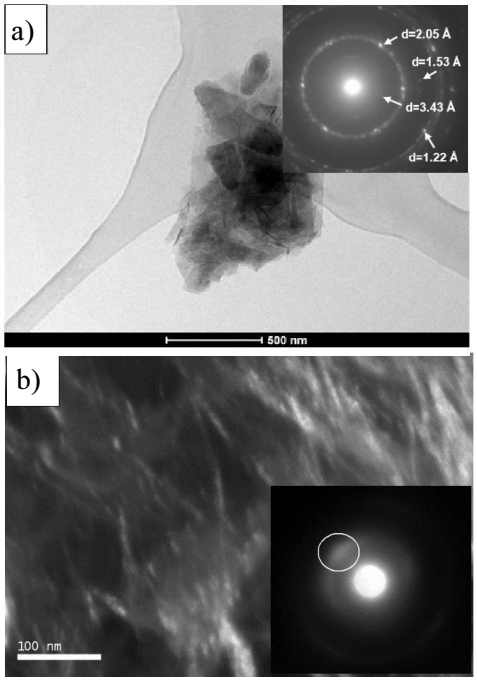

Fig. 1. TEM micrograph of N006 graphene platelet and electron diffraction pattern shown in insert (a); TEM micrograph of FLRGO platelets taken using dark field diffused reflection marked by white circle shown in insert (b)

Rys. 1. Mikrostruktura TEM z płytek grafenowych N006 i dyfrakcja elektronowa z widocznego obszaru zamieszczona w rogu (a); Mikrostruktura TEM płytek grafenowych FLRGO wykonana w ciemnym polu rozmytego refleksu 002 widocznego na dyfrakcji (b)

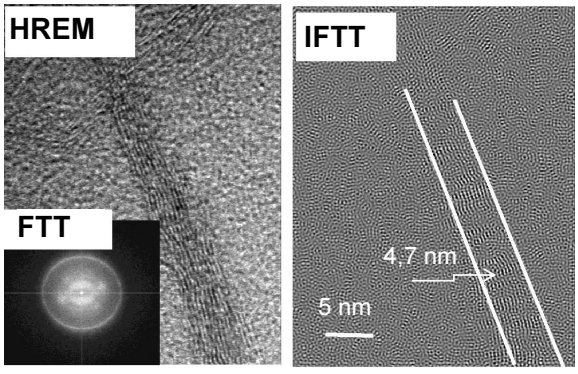

Fig. 2. HRTEM micrograph of graphene platelet with 002 plane oriented parallel to electron beam. In lower corner its Fourier transform (FFT) showing diffused ring from 002 graphite platelet plane and on right side inverse Fourier transform (IFFT) showing fringes from 002 plane in graphene platelet of thickness 4.7 nm in better contrast showing slight misorientation of platelet fragments

Rys. 2. Mikrostruktura wysokorozdzielcza z płytki grafenowej zorientowanej płaszczyznami 002 równolegle do wiązki elektronów. W lewym dolnym rogu transformata Fouriera (FFT) przedstawiająca rozmyty pierścień od płaszczyzn 002 płytki grafenu i po prawej odwrotna transformata Fouriera przedstawiająca prążki od płaszczyzn 002 w płytce o grubości 4,7 nm w lepszym kontraście z widoczną niewielką dezorientacją fragmentów płytek

The silver and graphene powders were mixed together by ball milling for 5 hours using a Pulverisette 5 Fritsch mill using zirconia containers and balls to avoid contamination during milling, with 0.5% stearin as the milling agent and applying a sample/ball weight ratio of 1:10. Composite samples 5 mm high and 20 mm in diameter were obtained after uniaxial hot pressing in alloyed steel containers. Additions in the amount of 1 or 2 wt.% of either N006 or FLRGO graphene were applied. Part of the powder was extruded at 400°C using heat resistant steel dies and a WC-Co carbide composite plunger (shown in Fig. 3) in a vacuum chamber.

Fig. 3. Die made from heat resistant steel with carbide plunger used for extrusion of Ag based 2% FLRGO graphene platelet composite

Rys. 3. Matryca wykonana ze stali żaroodpornej ze stemplem wykonanym z węglika spiekanego użytego do wyciskania kompozytu na osnowie srebra z dodatkiem 2% grafenu płytkowego FLRGO

Characterization methods

The structure and composition were studied using a Philips CM20 or FEI Technai G6 transmission electron microscope and a Quanta 3D FEG scanning electron microscope. Thin samples of graphene powders were observed on holey carbon foil, while those of the bulk samples were cut by a diamond saw, followed by dimpling using a Gatan dimpler and ion beam thinning in a Leica EM RES101 ion beam thinner. The hardness was measured using a Zwick ZHU 250 instrument. The electrical resistivity was measured using the 4 point contact method by a Keithley 2400 current source with a current supply of 100 mA to 1A at the precision of 1mA, and a Keithley 2182 nanovoltmeter.

RESULTS AND DISCUSSION

Figure 4 shows a set of SEM micrographs taken of hot pressed silver matrix composites containing 1÷2 wt.% of two kinds of graphene platelets; the coarser one N006, and the fine one FLRGO. All the samples show a low porosity below 0.5%, confirming the density measurements. One can see that the N006 graphene is mainly located at the silver particle boundaries, while FLRGO is distributed more uniformly, as well as inside the particles, however, in the sample containing 2%, the platelets are also often located at the particle boundaries, though, they do not form continuous layers. The changes in chemical composition measured using the EDS detector show a small increase in carbon content in the dark places in the micrograph, additionally confirming the accumulation of platelets at the particle boundaries.

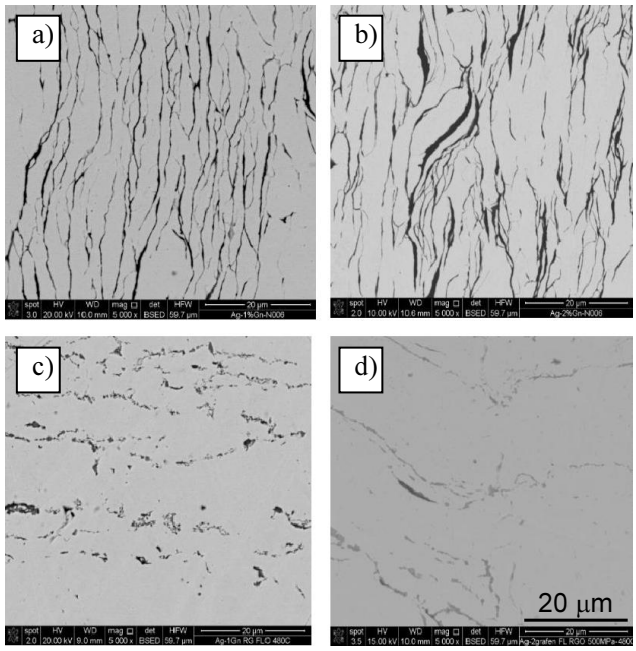

Fig. 4. SEM micrographs of silver matrix composites hot pressed in vacuum containing: a) 1% N006 graphene platelets, b) 2% FLRGO graphene, c) 1% FLRGO graphene, d) 2% FLRGO graphene

Rys. 4. Mikrostruktura SEM z kompozytu na osnowie srebra prasowanego na gorąco w próżni zawierająca: a) 1% grafenu płytkowego N006, b) 2% grafenu płytkowego N006, c) 1% grafenu płytkowego FLRGO, d) 2% grafenu płytkowego FLRGO

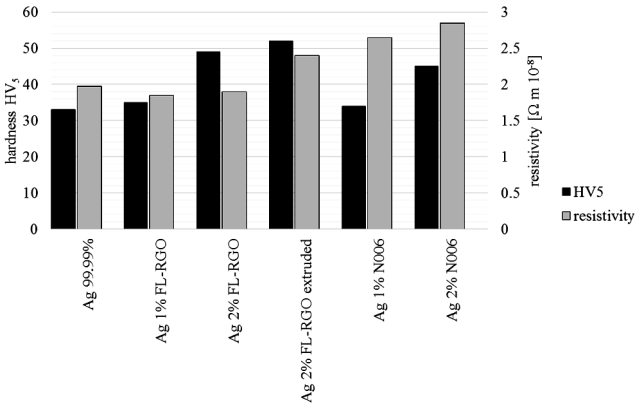

Fig. 5. Changes in hardness and electrical resistivity of hot pressed silver matrix composites containing either 1 or 2 wt.% N006 or FLRGO graphene platelets. Resistivity is only slightly higher in comparison with that of silver (1.59 10^{-8} W m)

Rys. 5. Wykres słupkowy prezentujący zmiany twardości i oporności elektrycznej prasowanych na gorąco kompozytów na osnowie srebra zawierających 1% wag. lub 2% wag. grafenu płytkowego N006 lub FLRGO

Figure 5 shows the hardness and electrical resistivity measurement results of the investigated composites with 1 and 2 wt.% additions of N006 and FLRGO graphene platelets. The resistivity of the composites is similar for the additions of 1 and 2% and only slightly decreases in comparison to that of hot pressed silver ($1.97 \cdot 10^{-8}$ Ω m) for the FLRGO additions. It is insig-

nificantly higher than that reported for bulk pure silver ($1.59 \cdot 10^{-8}$ Ω m) due to possible oxidation of the powder. The higher increase in resistivity in the composite with the N006 platelets is most probably caused by the higher resistivity of thicker platelets, as suggested in [11], where the electrical resistivity decreased with increasing thickness of the graphene films, which was also attributed to improved orientation and structure of the film, however, for films 10÷90 nm in thickness, thicker than those used in the present work. The hardness increases similarly for both types of platelets and the results coincide with that of copper based composites [10], where the finer platelets caused higher hardness of the composites. Figure 6 shows a TEM micrograph and SADP from the Ag-2% N006 graphene composite. One can see elongated bright islands of graphene plates consisting of several platelets cut perpendicularly to the plate surface i.e. 002 graphite planes. The diffraction pattern from the platelets and silver grains are diffused along the Debye-Scherrer rings indicating misorientation of the platelets and silver grains which occurred during milling and hot pressing. The presence of weak higher order reflections (also in rings) indicates the existence of graphite. One can also see some dislocations within the silver formed during hot pressure treatment and hot deformation of the silver during compaction. The next set of TEM micrographs taken of the silver matrix composite containing 2% FLRGO graphene is shown in Figure 7. It shows the graphene part of the composite consisting of curved bands of platelets of a thickness of several nm. The dark field micrograph (Fig. 9b) taken using diffused reflection from graphene (shown in diffraction in the insert), allows one to distinguish small shining areas within the individual bands, which means that the crystals within the bands are slightly disoriented similar to the initial graphene platelets in Figures 1 and 2 and similar to the observed lateral size of crystals within the FLRGO graphene platelet bands in copper/graphene composites using Raman spectroscopy [10].

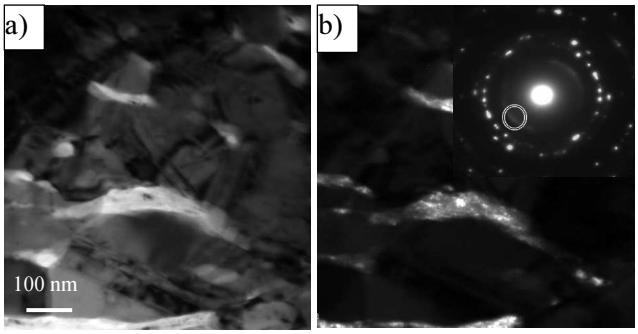

Fig. 6. TEM micrograph of silver based composite containing 2% N006 graphene (a); Dark field image taken using diffused reflection of elongated graphene platelet marked with white circle in electron diffraction pattern shown in insert (b)

Rys. 6. Mikrostruktura TEM kompozytu na osnowie srebra zawierającego 2% grafenu płytkowego N006 (a); Mikrostruktura w ciemnym polu wykonana za pomocą rozmytego refleksu 002 grafitu zaznaczonego białym okręgiem na dyfrakcji z widocznego obszaru przedstawionej w dolnym rogu (b)

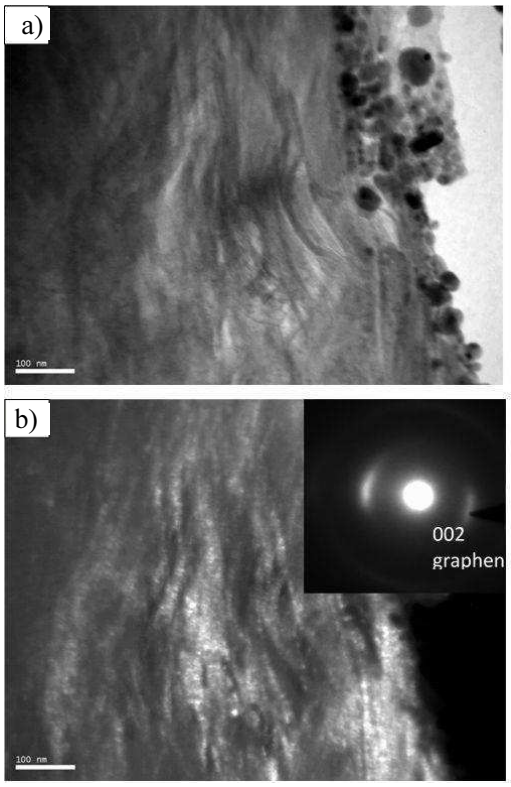

Fig. 7. TEM micrograph in bright field of silver based composite with 2% FLRGO graphene platelets (a); Dark field micrograph showing bright lamellar graphene taken using basal plane diffused 002 graphene reflection visible in diffraction pattern shown as insert (b)

Rys. 7. Mikrostruktura TEM w jasnym polu z kompozytu na osnowie srebra zawierającego 2% płytek grafenowych FLRGO (a); Mikrostruktura wykonana w ciemnym polu przedstawiająca jasne pasma grafenu, uzyskana przy pomocy rozmytego refleksu 002 płaszczyzny podstawy grafenu widocznego na dyfrakcji elektronowej zamieszczonej w rogu (b)

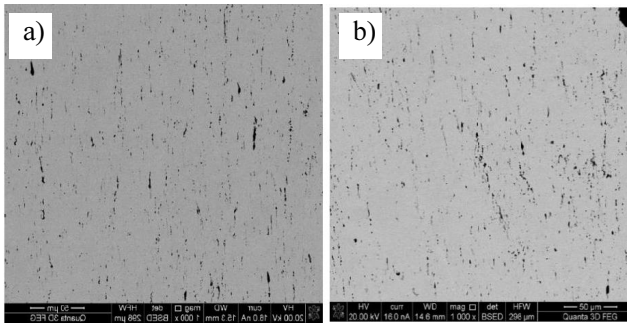

Fig. 8. SEM micrographs of hot pressed and extruded Ag-matrix composite containing (a) 1% FLRGO graphene platelets and (b) 2% FLRGO graphene platelets

Rys. 8. Mikrostruktura SEM z kompozytu na osnowie srebra prasowanego na gorąco, a następnie wyciskanego na gorąco zawierającego (a) 1% płytek grafenowych FLRGO i (b) 2% płytek grafenowych FLRGO

Figure 8 shows SEM micrographs of hot pressed, extruded Ag-FLRGO graphene composites containing 1 and 2% FLRGO graphene. One can see that the platelets show a similar structure as in the only hot pressed material, however, they seem to be coarser and aligned along the pressing direction. The TEM micrograph shown in Figure 9 is also similar to that from Figure 6

of only hot pressed material, however, the graphene platelets are coarser, which is confirmed by electron diffraction where the 002 reflections are less diffused indicating a larger grain size.

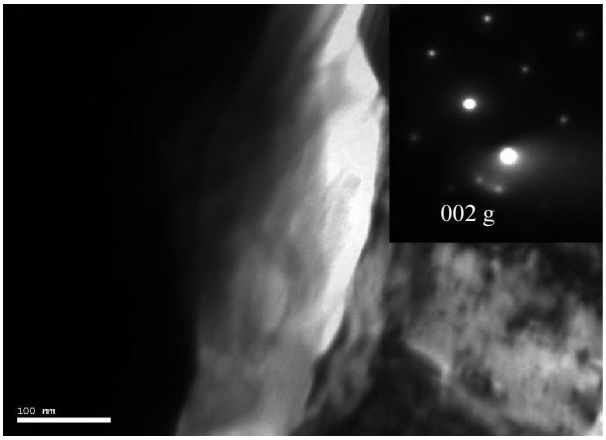

Fig. 9. TEM micrograph of hot pressed and extruded silver based composite and electron diffraction pattern from the area of micrograph shown as an isert

Rys. 9. Mikrostruktura TEM prasowanego na gorąco, a następnie wyciskanego kompozytu na osnowie srebra i dyfrakcja elektronowa z obszaru widocznego na mikrostrukturze zamieszczonej w rogu

CONCLUSIONS

1. Hot pressing in vacuum allowed the authors to obtain composites of a low porosity containing 1÷2% graphene platelets. The addition of fine FLRGO graphene with a platelet thickness of 2÷4 nm in the amounts of 1 and 2 wt.% led to a similar hardness as in the case of the N006 platelets, however, it shows similar electrical resistivity to that of pure hot pressed silver. The addition of coarser N006 platelets caused a resistivity increase up to about a 40% higher value than that of pure silver. Hot extrusion caused an additional hardness and electrical resistivity increase.
2. The SEM studies of the hot pressed composites from the ball milled powders have shown a slightly more homogeneous microstructure of the samples with the fine FLRGO graphene additions than those with N006 where the graphene was distributed at the deformed silver particle boundaries. Hot extrusion caused directional alignment of the platelets in the extrusion direction and slight coagulation of the platelets.
3. The TEM studies enabled the authors to determine an insignificant change in the structure of the platelets after hot pressing. In the initial and in the hot pressed state, the platelets were composed of curved bands of a thickness up to several nm and a lateral size of a few nm. Refinement of the silver particles down to a few nm was observed near the silver/graphene interfaces where plastic deformation of the silver particles allowed mixing of the nanocrystalline silver and graphene phases. The platelet conglomerates gave diffused electron diffraction due to the thickness and lateral size of a few nm. Extrusion caused growth of the graphite crystals within the platelets, resulting in changes in the character of the electron diffraction pattern and causing an increase in electrical resistivity.

Acknowledgements

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