The manufacturing and properties of a nano-laminate derived from graphene powder

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Łukasz Zych[*], Paweł Rutkowski, Ludosław Stobierski, Dariusz Zientara, Krzysztof Mars, Wojciech Piekarczyk

Faculty of Materials Science and Ceramics, AGH-University of Science and Technology, al. Mickiewicza 30, 30-059 Krakow, Poland

ARTICLE INFO

ABSTRACT

The work presents a method of consolidation of graphene flakes (platelets) into a bulk material showing high anisotropy of thermal, electrical and mechanical properties. Such materials can be used as directional high-temperature thermal insulators similar to graphite foils, but due to much finer microstructure they may exhibit different, possibly enhanced properties. The graphene flakes were consolidated by a filter pressing of propanol suspension followed by a hot-pressing of produced green bodies at 2200 °C under 25 MPa in a protective atmosphere.

The hot-pressing step was necessary to force orientation of the flakes and to densify the material. Microstructural observations, mechanical strength and elastic properties assessment, as well as thermal and electrical properties analysis were performed. Scanning electron microscopy revealed that microstructure of the material consisted of highly-oriented layers of the graphene flakes. It resulted in a distinct anisotropy of thermal conductivity (360 vs. 3 W/mK), coefficient of thermal expansion ($25 \cdot 10^{-6}$ vs. $-1 \cdot 10^{-6}$ 1/K) and electrical resistivity ($60 \cdot 10^{-6}$ vs. $850 \cdot 10^{-6}$ Ω m) of the material in the in-plane and through plane direction, respectively. The material showed brittle behavior, but it could be machined.

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1. Introduction

Graphene is monoatomic layer of carbon atoms showing interesting mechanical, thermal end electrical properties [1–3]. It can also have a form of platelets (flakes) of few micron lateral size consisting of a few layers of carbon atoms. They can be used for example as a reinforcement (filler) of composites with polymer, metallic or ceramic matrix [4]. Depending on the composite matrix type it can increase its toughness, improve its thermal or electrical conductivity etc. [5–8]. Graphene flakes can be used alone, sometimes modified, for example to production of conductive paper [9], porous chemical sensors [10], gas storage etc. According to our best knowledge, in the literature there is only one example of production of a bulk, dense materials from graphene flakes. Nieto et al. reported on consolidation of graphene flakes by spark plasma sintering (SPS) method, and mainly focused on evaluation of structural and mechanical properties of the bulk graphene-derived material. The graphene-derived material reflected mechanical

properties of graphene flakes used as reinforcement in ceramic matrix composites prepared for example by SPS method [11]. The main goal of our studies was elaboration of a method of production of bulk, dense materials based on graphene flakes showing distinct anisotropy of thermal conductivity, resulting from laminar alignment of graphene flakes during processing. The materials should have useful sizes and mechanical strength sufficient to handling and machining.

One of problems related to consolidation of graphene powders is their low bulk density (i.e. a density of a powder loosely poured into a container) in the range of 0.1 g/cm³, making them difficult to consolidate using dry powder techniques for example by uniaxial pressing. We think that such materials could be used as anisotropic thermal insulation similar to commercially available graphite foils. According to available data form the producers, thermal conductivity along the graphite foil surface (in-plane direction) vs. conductivity through the foil (through plane direction) can be as 200 vs. 4 W/m·K. Obviously, the graphene-derived material could not compete with commercial graphite foils on the price level, but because of application of graphene flakes which are much finer than particles of expanded graphite some different characteristics of the material can be expected. The developed method is general,

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* Corresponding author.
E-mail address: lzych@agh.edu.pl (Ł. Zych).

and be used to consolidation of different grades of graphene flakes.

2. Experimental

Graphene powder A0-3 (Graphene Laboratories Inc., USA) in the form of flakes was used. According to the producer an average lateral size of the flakes was 4.5 μm (1.5–10 μm) and their thickness was 12 nm which corresponds to 30–50 graphene monolayers. Phase analysis and of the powder was performed by X-Ray diffraction method (XRD) using X'PERT-PRO (PANalytical) equipped with Cu lamp. The measurements were performed in 5° to 60° 2Θ range with a step of 0.008° (2Θ). Crystallite size L_C was calculated from (002) line broadening using the Sherrer's formula [12].

The graphene powder was observed using Transmission Electron Microscope (TEM, JEM-1011, Jeol Inc.). Specific surface area of the graphene flakes was measured using the Brunauer–Emmett–Teller surface area analysis (BET, Nova 1200e, Quantachrome Instruments, USA). The measurements were performed using nitrogen as adsorbate, and adsorption took place in the standard BET range. Before the measurement the powder was evacuated overnight at 300 °C under vacuum of 0.05 mbar.

True density (i.e. density of a material without pores) of the graphene flakes was measured using helium pycnometer (Accupyc II 1340, Micromeritics Inc.) using 70 purges of helium. Before the measurement the graphene powder was evacuated overnight at 300 °C under vacuum of 0.05 mbar. The result was an average of 30 measurements.

Bulk density of the graphene powder was measured by weighting a known volume of the powder. The graphene flakes were ultrasonically dispersed in 5 wt.% phenol-formaldehyde resin solution. The solution was prepared using MR Novolac resin (Organika-Sarzyna s.a., Poland) and isopropanol alcohol (POCh, Gliwice, Poland). The resin was used as temporary binder, bonding the graphene flakes during their consolidation process, and then removed (carbonized) during high-temperature treatment. Concentration of the graphene flakes in the prepared suspensions ranged between 2.5 and 8 wt. % which approximately corresponded to 1 and 3 vol. %, respectively. It should be noted, that it was the maximum concentration of the suspension at which it was pourable. The suspension was not stabilized by any means, so probably the concentration of the graphene flakes could be increased. The graphene flakes were dispersed in propanol using high-energy ultrasonic disintegrator for 5 min.
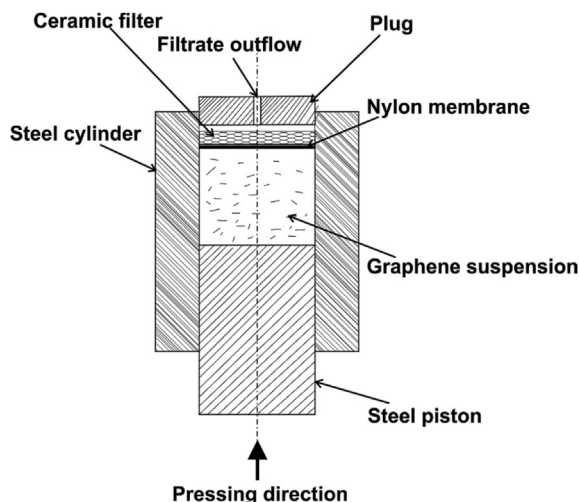
The suspension was poured into a steel chamber of a filter press presented in Fig. 1. The press can be equipped with steel chambers of 30 or 55 mm diameter. Both of them were successfully used to consolidate the graphene flakes, but for the test purposes smaller chamber was chosen and the presented results are related to samples of 30 mm diameter.

The suspension was pressed with a steel piston against ceramic filter covered with a nylon membrane with 0.45 μm pore diameter (Whatmann Inc.). The applied pressure was 5 MPa and it was maintained constant until filtrate leakage stopped. The pressure was generated by a manual hydraulic pomp [13].

The filter-pressed compacts were dried at room temperature in a desiccator over silica gel for 24 h, and then in a dryer at 100 °C for 3 h. This preparation step allowed consolidation of the graphene flakes into compacts with mechanical strength sufficient to manipulate them during further processing. Apparent density (i.e. density of a material including pores) of the compacts was determined by their weight and geometrical dimensions. Thickness of the compacts was c.a. 8.5 mm, and in order to prepare sufficiently thick final bodies two compacts were placed in a graphite die of 30 mm diameter. Surfaces of the graphite die and punches were covered with a graphite foil of 1 mm thickness (Sigraflex Z, SGL Carbon).

The hot-pressing (HP) was performed in HP50-7010G press (Thermal Technology Inc., USA) under 25 MPa pressure at 2200 °C under argon flow. Heating ramp rate was 10 °C/min and dwell time at the maximum temperature was 30 min. The chosen conditions of the HP processing were the maximum temperature and pressure supported by the press, in order to assure the highest densification and the best alignment of the graphene flakes. For this moment the conditions of production of the nanolaminates were not fully optimized.

After the hot-pressing remains of the graphite foil were removed from the material surfaces, and the samples were cut using a precision cut-off machine (Accutom 50, Struers) into smaller pieces with dimensions suitable for further studies. Main properties of graphitic materials i.e. apparent density, Young's modulus, flexural strength, thermal conductivity, coefficient of thermal expansion and electrical resistivity were characterized [14]. We suspected, that the material may show anisotropy in a direction parallel to the applied pressure which was denoted in a further text as a "through-plane direction" and in a direction perpendicular to the applied pressure which was denoted in the text as an "in-plane direction". Schematic view of a sample with the distinguished directions was shown in Fig. 2.

Apparent density of the samples were measured using the Archimedes principle (i.e. the hydrostatic weighting in water). The method is used to measure an apparent density of a sample, but if a true density (helium density or theoretical density) of the material is known total porosity of the sample can be calculated as well as it is possible to distinguish between open and close porosity. Prior to the measurements the samples were soaked with water under vacuum for 2 h at room temperature. The sample had open pores because it gained some measurable amount of water during this step. Then the sample was weighted in water and then weighted in
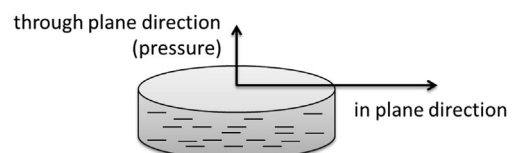

Fig. 1. Schematic view of the filter pressing apparatus.

Fig. 2. Schematic view of a sample with distinguished directions of measurements.