Graphene nanocomposites as thermal interface materials for cooling energy devices

A S Dmitriev, A R Valeev
National Research University “Moscow Power Engineering Institute”
Russia, 111250, Moscow, Krasnokazarmennaya 14
asdmritiev@mail.ru

Abstract. The paper describes the technology of creating samples of graphene nanocomposites based on graphene flakes obtained by splitting graphite with ultrasound of high power. Graphene nanocomposites in the form of samples are made by the technology of weak sintering at high pressure (200-300 bar) and temperature up to 150 °C, and also in the form of compositions with polymer matrices. The reflection spectra in the visible range and the near infrared range for the surface of nanocomposite samples are studied, the data of optical and electronic spectroscopy of such samples are given. In addition, data on the electrophysical and thermal properties of the nanocomposites obtained are presented. Some analytical models of wetting and spreading over graphene nanocomposite surfaces have been constructed and calculated, and their effective thermal conductivity has been calculated and compared with the available experimental data. Possible applications of graphene nanocomposites for use as thermal interface materials for heat removal and cooling for power equipment, as well as microelectronics and optoelectronics devices are described.

1. Introduction
Thermal interface materials (TIMs) play an important role in the electronic components area due to the continued miniaturization and lightweight [1-7]. As a novel material with a thermal conductivity as high as 5000 W/m·K, graphene is regarded as a promising filler to improve the thermal performance of the TIMs. In this study, graphene flakes obtained by splitting graphite with ultrasound of high power. Experimental and calculated results manifest a strong coupling of phonon modes between graphene and the matrix. The influences from graphene on thermal conductivity of composites are discussed. Larger size graphene sheets and surface functional groups would further reduce the Kapitza thermal resistance between the interfaces of graphene flakes. Moreover, the tested mechanical properties demonstrate that adding of graphene does not influence the outstanding mechanical performance of the matrix.

2. Method for manufacturing graphene tablets and their properties
To study some properties of the obtained graphene powder and to reveal various thermophysical, electrophysical and optical characteristics, it was decided to make the tablets by pressing the graphene powder. The method is a physical pilling of the original natural graphite. The yield of the product is 99% of the feedstock. In the process, only the discile is used, no surfactants or oxidants are used. The high yield of the product is due to the selection of combinations of the parameters of the installation: the ultrasonic radiation power at the end of the full waveguide, the high amplitude of the waveguide end shift, the design of the flow ultrasonic reactor, the high static counterpressure, the processing temperature, the ultrasonic frequency, and its cascade increase. The combination of these parameters made it possible to obtain an average energy density in the reactor up to 20 MW/m². In this process, the so-called “separation of graphene plates from the initial graphite” does not occur. The method consists in stratifying graphite by shifting the graphene plates relative to each other. This solution greatly simplifies the operation and study of the properties of graphene powder, since it does not require constant selection of a constant volume between the experiments. The production of tablets was carried out with the help of an automatic machine for hot pressing the Buehler SimpliMet 1000 (Figure 1).
The production takes place in two stages: 1) the choice of a certain volume of graphene powder, on which the thickness of the obtained samples depends; 2) loading the selected volume of powder into the press for further pressing. The choice of a certain volume of powder is carried out by a conventional 20 ml medical syringe. To do this, the end of the syringe is carefully cut along the first line of the calibration. As a result, a large hole is obtained equal to the diameter of the syringe, with which it is already possible to easily obtain the required volume of graphene powder. The collected volume of graphene is pushed out by the plunger of the syringe into the mold, which is closed with a plug on top. Then, the press-fitting parameters are selected on the control panel of the press and then the process is started. At the end of the process, a cap is opened and a mold with a received graphene tablet is lifted using the control buttons. For this work, samples of graphene tablets were made at various press parameters and various powder volumes. As a result, samples of different thicknesses were obtained. Pressures of 200 and 300 bar were used in the manufacture. At each pressure value, 3 samples of different thicknesses were made. The thickness depended on the amount of graphene powder used. The measurement of quantity was carried out in volumetric units with the help of a syringe, which allowed to measure a certain amount and was convenient for loading the metered powder into the mold. Since this press is a highly specialized equipment, intended mainly for metallographic research, it constantly heats the material loaded in the mold. Therefore, the lowest possible temperature of 150 °C was used for manufacturing. As it was said above, 3 samples were prepared for each pressure value with powder volumes equal to 2, 5 and 10 ml respectively. Different values of pressure and volume gave different thicknesses of the obtained samples (Figure 2).

3. Measurement of the degree of reflection of graphene tablets
In the process of manufacturing graphene tablets, it was observed that all the samples obtained had a smooth and fairly developed reflective surface. Therefore, first of all it was interesting to study the...
samples for optical properties. Using the microscope Motic DM-1802, optical images of the surface structure of the obtained samples of graphene tablets were obtained. The microscope allowed to take images of the structure of the surface at a magnification of 4 and 10 times. The obtained images are presented below in the photographs (Figure 3).

![Figure 3](image1)

The degree of reflection of the sample surface was also measured. Since the surface structure of all samples is similar to each other, a sample with less mechanical damage (sample No. 6) that occurred during the operation of graphene tablets underwent a measurement of the degree of reflection. The investigations were carried out using the Avantes AvaSpec-2048XL spectrometer. The image below (Figure 4) shows the results of the dependence of the degree of reflection on the wavelength incident on the sample under study. As seen from the diagram, in the visible part of the spectrum, the degree of reflection lies in the range of 5-10%. In the longer-wave part, infrared, reflection increases to 20-25%.

![Figure 4](image2)

The minimum degree of reflection is observed in the wavelength range 450-550 nm. These indicators are quite low compared to other substances, although as mentioned earlier, visually the samples appear more reflective, which is especially noticeable in photos taken with a microscope, where the incident light is reflected both from the metal surface.

4. Investigation of the properties of graphene thermal greases

Investigation of the properties of graphene thermal grease includes experiments on the measurement of thermal conductivity by two methods: the method of thermal resistance of a layer of graphene thermal grease and the method of laser flash (LFA-laser flash analysis). The laser flash method is a more accurate method, so the results of these methods will be compared with each other. Also, in this chapter, we will give the results of a comparison of the characteristics of heat conducting pastes: graphene and
silicone paste with ceramic filler. The comparison is made under operating conditions, on a working processor from AMD. In all experiments, graphene thermal grease with different graphene content by volume is used: \( f \approx 15, 20 \) and 30%. Figure 5 shows the dependence of thermal conductivity of thermal grease on the volume content of graphene filler in it. The diagram shows that the value of the thermal conductivity of the first paste is lower than that of the others. In this case, the volume fractions of graphene of the first and second samples differ by only 5%, with a difference in their thermal conductivity of almost 2 times (\( \sim 1.923 \text{ W/m-K} \)). For comparison, the difference in the thermal conductivity of the second and third sample is only 0.195 W/mK, with a difference in the volume fraction of graphene in the grease compositions by 10%.

![Figure 5.](image)

The laser flash method is one of the most accurate methods for determining the thermal conductivity at the present time. As in previous experiments on the measurement of thermal conductivity by the thermal resistance of a layer, the thermal conductivity of the same graphene heat conducting grease was measured by the laser flash method.

![Figure 6.](image)

Therefore, you can compare these methods, and determine how accurate the measurement results in the first method are relative to the second method. It is important to note that measurements of the
laser flash method measured not the thermal conductivity $\lambda$, but the thermal diffusivity of the sample $\alpha$, whose values are used to calculate the thermal conductivity. Figure 6 presents a comparison of the results of measurements of thermal conductivity by two methods.

5. Comparison of the characteristics of graphene and silicon organic thermal grease with ceramic filler

In this series of studies, various heat-removal experiments have been carried out, differing in cooling type (passive and active) with heat-conducting graphene thermal greases. However, it should be noted that the experiments were carried out with only one graphene thermal grease, with the greatest thermal conductivity, which was compared directly with commercial paste. In these experiments, the thermal interface of the Titan company was used as the thermal interface (TTG-G30015). But before carrying out experiments with thermal greases, experiments were conducted to identify the average temperature of the processor's heating, in order to compare with this temperature the values obtained during the basic heat removal experiments to assess the efficiency of the greases. The experiments were performed on an AMD processor with Titan thermal grease applied to it (Figure 7a).

Experiments with graphene heat conducting grease were carried out in the same way as experiments with commercial Titan thermal grease. Also, several experiments were carried out, differing in the cooling type, and at the end of each experiment a measurement was made of the cooling rate of the processor after operation.
During the preparation of the experiment, it was noticed that this thermo-paste has poor adhesion, it was poorly applied to the surface of the crystal and adhered to lumps, which made it difficult to apply it in a thin layer. This problem was solved by applying a thicker layer of thermal paste and further squeezing it from the center of the crystal to its edges. Surplus pastes from the edges were carefully removed and a relatively thin layer remained on the crystal. The result of applying the paste is shown in Figure 7b.

Analyzing the main characteristics of the examined and experimentally studied thermal interfaces, the following results were obtained: the thermal paste Titan does a little better than its heat conductive paste with graphene filler, but the latter observed more uniform thermal conductivity, which does not cause temperature fluctuations. The established temperature regime for graphene thermo-paste began already at 200-400 s, when the commercial Titan paste did not observe a steady-state regime at all. It was also noticed that the cooling of the processor after operation is much faster when using a heat-conducting paste with graphene filler.

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