The heat storage material based on paraffin-modified multilayer carbon nanotubes with Nickel-zinc ferrite

A Shchegolkov[1], A Shchegolkov[1], T Dyachkova[1] and A Semenov[2, 3 *]

[1] Tambov State Technical University, Tambov, 392000, Russia
[2] Institute of Space Technologies, People's Friendship University of Russia (RUDN University), Moscow, 17198, Russia
[3] Moscow Technological Institute, Moscow, 119334, Russia

*E-mail: semenov.venture@mail.ru

Abstract The paper presents an investigation of magnetically controlled heat-storage material based on paraffin, modified with multilayer carbon nanotubes with nickel-zinc ferrite. The technology of obtaining nanomodified material capable of interacting with magnetic field is presented. The study of the heat-exchange processes of charge/ discharge with the help of magnetic field are carried out.

1. Introduction.

The development of modern materials science is associated with the emergence of technologies for the production of "smart" materials possessing special functional properties and capable of adapting to various environmental conditions. Heat-storage materials may take on special importance in the hierarchy of creating "smart" materials. Heat-storage materials can be widely used in aerospace engineering, power engineering, as well as for heat-loaded elements of power and computer electronics. For aviation important is reliability and minimum mass-dimensional parameters. As the directions of application of heat-storage materials, it is possible to isolate electronic power components, microclimate thermal control systems, electric energy storage systems, especially if they are built on the basis of lithium-ion and polymer batteries. The ability to absorb thermal energy for such materials is a consequence of the accumulation of heat as a result of a phase transition. As a rule, these are phase transitions in the range from 40 to 120 ° C. Recently, heat-storage materials are actively used as the basic elements of thermal interfaces. Such thermal interfaces can be used to thermoregulate lithium-ion and lithium-polymer batteries. This concerns both portable systems and powerful storage stations for renewable energy and electric transport. This is the direction of scientific research. It was proposed in [1] to use the material to change the thermophysical parameters of paraffin by using graphene. The aim of the work was to improve the performance of lithium-ion batteries due to the reduction of the negative effect of self-heating. In [2], the effectiveness of the discharge efficiency of a lithium cell at various operating temperatures (15-45 ° C) was estimated by the thermal model. Numerical results were compared with experimental data obtained from laboratory studies. In [3], a comparison was made between the internal and external cooling procedures for thermal control. They performed a two-dimensional and three-dimensional transient temperature analysis of a prismatic lithium-ion battery. Consider the prospects for using nanomaterials for phase transition materials using the example of theoretical work [4, 5]. In [4], to improve the properties of

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paraffin, a theoretical substantiation of nanocrystals of graphene, garnet nanoplates, and nanomembranes h-BN is carried out. Thermal conductivity of paraffin with 1% and 4% vol. Is considered. Concentrations of these nanofillers. In this case, the thermal conductivity of paraffin with fillers was 0.3 W / mK and 0.6 W / mK (0.36 W / mK and 0.65 W / mK). The paper [5] shows that the use of graphene in the phase-transition material makes it possible to increase its thermal conductivity by more than two orders of magnitude while retaining the latent ability to store heat. The use of this approach leads to a significant drop in temperature in a standard lithium-ion battery.

The paper [6] shows studies of the thermal conductivity of materials with a self-leveling effect in the structure of a modified material. A method for the synthesis of nanocomposite graphene with Fe_3O_4 nanoparticles is presented. Self-leveling of "magnetic graphene" improves the thermal conductivity of composites and epoxy resins. Improvement of thermal conductivity with oriented fillers occurs at low concentrations of the order of ~ 1%. In real time, testing with computer chips demonstrated a temperature decrease of 10 ° C using a material without a thermal interface with ~ 1 wt. % oriented fillers. At the same time, the authors of [7] consider materials that do not have a phase transition, which reduces their effectiveness in the case of intense heat fluxes. Questions arise with giving nanostructures magnetic properties. The functionalization of CNTs with the help of magnetic nanoparticles was investigated in Refs [7,8]. The influence of orientation and alignment of carbon nanotubes (CNTs) embedded in an epoxy polymer matrix under the action of a magnetic field on the mechanical properties of the nanocomposite obtained was studied in [7,8]. The authors found that when alignment of CNTs occurs in fact in high magnetic fields, the properties of the composites obtained exceed properties that were not subjected to a magnetic field. So in [7,8] physicochemical mechanisms are investigated under which positive charges ensure effective adsorption of negatively charged magnetic nanoparticles on the surface of graphene by means of electrostatic interactions. The adsorption of nanoparticles (diameter D ~ 6-10 nm) on graphene surfaces is more effective than on CNT surfaces due to the high curvature of CNTs, which prevents the formation of dense coatings. Magnetic nanoparticles obtained in solution (basic pH) are negatively charged and therefore are electrostatically attracted to the positively charged layer of poly-dimethyl-diallylammonium chloride adsorbed on graphene fillers. For the CNT, the authors of Ref. [7] established that the pH for the most effective adsorption of Fe_3O_4-ɣ-Fe_2O_3 nanoparticles on polyelectrolyte was found to be pH = 11.9-12.0 [8]. Hybrid materials based on maghemite (γ-Fe_2O_3) / multilayer carbon nanotubes (MWCNT) were synthesized in [9] and their anisotropic electrical conductivities were investigated as a result of their equalization in a polymer matrix under an external magnetic field. Modification of γ-Fe_2O_3 nanoparticles on the MWCNT surface was achieved by a modified sol-gel reaction in which sodium dodecylbenzenesulfonate (NaDDBS) was used to inhibit the formation of a 3D iron oxide gel. These hybrid materials, in particular magnetized multi-walled carbon nanotubes (m-MWCNT), were easily aligned parallel to the direction of the magnetic field even when a weak magnetic field was used. However, such methods of functionalization were considered in the framework of applied problems aimed at changing the strength and electrical conductivity of polymers. In this connection, it is necessary to consider the possibility of obtaining efficient heat-storage materials with improved thermophysical properties and adapted for use in aeronautical engineering. Heat-accumulating materials for aviation equipment should have functionality by using additional materials that react to the magnetic field. The possibility of interaction with a magnetic field, which will acquire nanomodified heat-accumulating material, will provide an opportunity to regulate internal heat exchange. This will allow you to control the charge and discharge modes of the thermal battery, which will be based on magnetically controlled heat-accumulating material, which will make the material more compact and provide a reduction in mass-dimensional parameters. In addition, the problem of moving layers of high-temperature layers with a lower temperature regime of convective heat transfer will be considered.

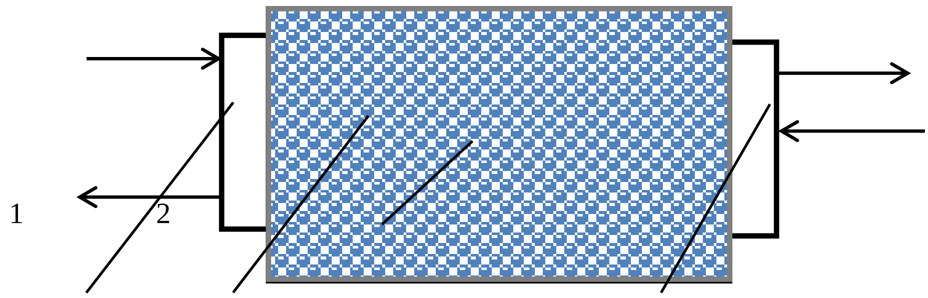
2. Methodology and materials

To implement the tasks set, the technology of directed synthesis of multilayer carbon nanotubes was used. The introduction of MWNTs (multilayer carbon nanotubes) into paraffin was carried out with the help of ultrasonic radiation and exposure to magnetic fields (up to 1500 mT). Within the framework of directed production of carbon nanotubes, the synthesis of Mo-Al_2O_3-MgO and Ni-MgO catalysts was carried out. After that, MWNTs were mechanically activated with nickel-zinc ferrites 400NH Ni1-xZnxFe_2O_4 with preliminary crushing to 2-4 microns in a ball mill for 60 minutes. Subsequently, the resulting carbon nanotubes were used to modify paraffin P-2 (Lukoil, Russia).

The modification of paraffins obtained by (multilayer carbon nanotubes) with the necessary morphology provides interactions at the molecular level and creates a stable material with the characteristics that are necessary for the formation of TM. The modification occurs during the phase transition of paraffin, when it passes into the liquid state at the temperature at which the threshold of its thermal decomposition is reached, which allows the reactivity of MWNTs with paraffin molecules to initiate this process. The application of ultrasonic radiation (2 kW power) made it possible to create cavitation in the volume of liquid paraffin (at a temperature of 90-95 ° C).

To ensure the necessary orientation of the structures integrated in the MWNTs, the molten paraffin was exposed to a magnetic field during cooling. After that, the material was placed in the extruder using a fluoroplastic screw. The power of the drive motor of the extruder is 2 kW at a speed of 100 rpm. In addition, the resulting material was granulated in a compacting granulator to form granules to a size in the range of 0.5 to 1 mm. After this operation, the granules were placed in a carrier fluid. The carrier fluid was a synthetic motor oil CASTROL 0W30. Motor oil and magnetic filler were weighed on the Unit G-200 scales with an accuracy of ± 5 mg. After this, the filler was introduced into the engine oil and mixed thoroughly. The resulting thick slurry was diluted with a carrier liquid and mechanically stirred until a colloidal solution was obtained. As a result, the liquid phase - motor oil was 20%, and the solid phase - nanomodified composite - 80%.

Figure 1 shows an experimental model for the study of charge / discharge in magnetically controlled heat-accumulating material.



Where 1 - input heat exchanger, 2 - vessel c in magnetically controlled heat-accumulating material distributed in industrial oil, 3 - magnets 4 - output heat exchanger

Figure 1. Experimental model for charge / discharge research in magnetically controlled heat-accumulating material

The heat flux source is located in the lower part of the tank in the form of a flat electric heater with a power of 300 W and an area of 0.003 m^2. With such heater parameters, the heat flow is 100 kW / m^2

Research results Preliminary test for interaction with a magnetic field (Fig. 2) Fig. 2 A shows the heat-accumulating composite before the action of the magnetic field, and in Fig. 2 B after exposure.

Figure 3 shows the distribution of the temperature field, taking into account the effect of the magnetic field at the end part of the heating battery.

Figure 4 shows the distribution of the temperature field with allowance for the effect of further movement of the magnetic field.

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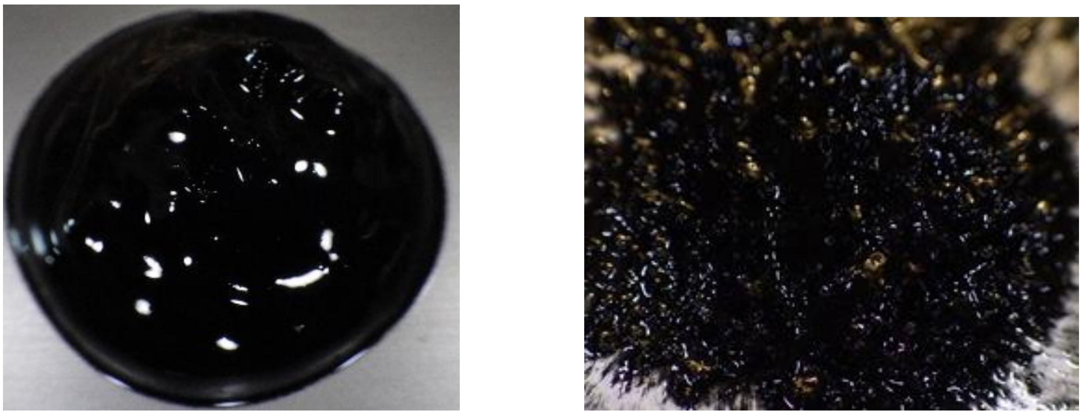

A) B)

Figure 2. Ferromagnetic liquid under the action of a magnetic field.

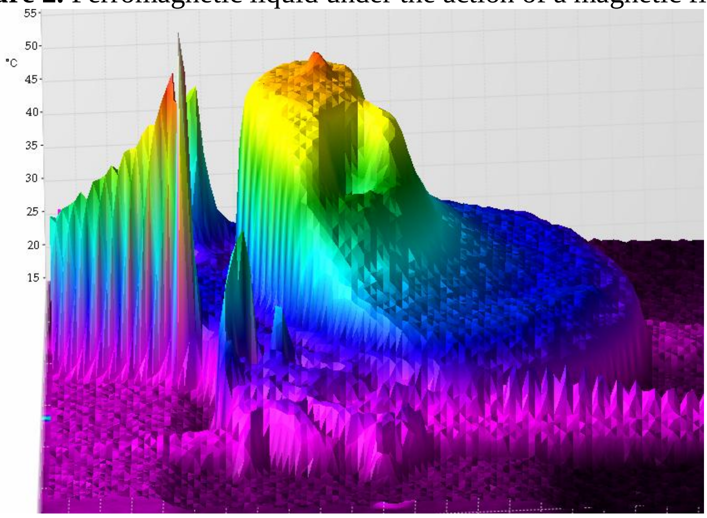

Figure 3. 3-dimensional thermogram of magnetically controlled heat-storage material

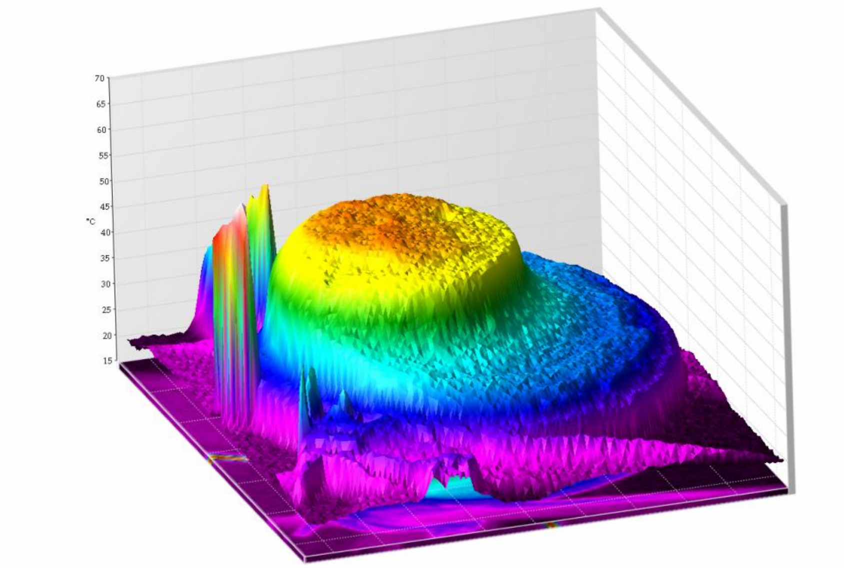

Figure 4. 3-dimensional thermogram of magnetically controlled heat-storage material.

Figure 5 shows the distribution of the temperature field with allowance for the effect of the magnetic field over time - 10 s.

Figure 6 shows the distribution of the temperature field taking into account the effect of the magnetic field over a period of 25 s.

Figure 7 shows the distribution of the temperature field taking into account the effect of the magnetic field over a period of 45 s.

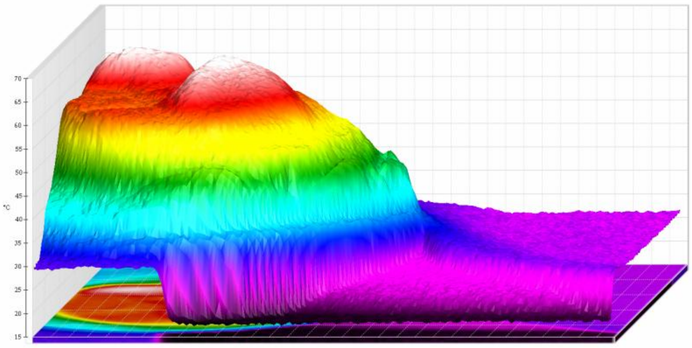

Figure 5. 3-dimensional thermogram of magnetically controlled heat-storage material

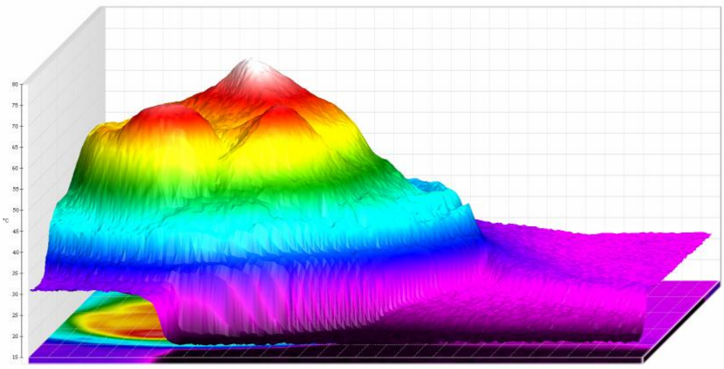

Figure 6. 3-dimensional thermogram of the magnetically controlled heat-storage material.

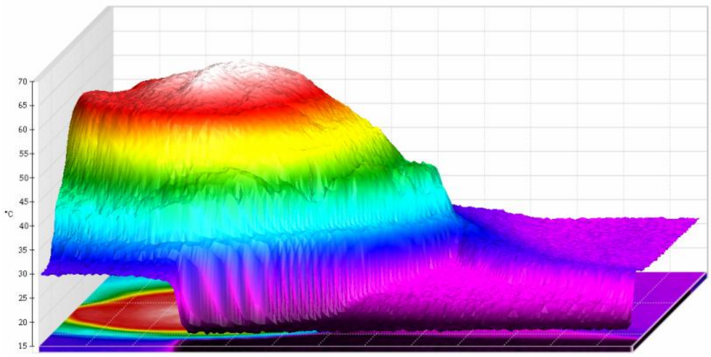

Figure 7. 3-dimensional thermogram of magnetically controlled heat-storage material

3. Discussion of the results

Figure 3-7 shows the distribution of the temperature field in the container containing the nanomodified paraffin with ferromagnetic particles distributed in the synthetic oil, as a result of the action of the magnetic field of the cylindrical shape created by the permanent magnet. To intensify the process, a permanent magnet is used, which creates a magnetic field in a specific part of the container and causes TM to travel to this part of the container. In the case of mechanical displacement of the magnet, the intensity of heat exchange increases, since it becomes possible to transfer hot and cold layers. The subsequent equalization of the temperature field from the state (Fig. 6) with an explicit temperature peak is due to intrinsic thermal conductivity (Fig. 7). At the end of the charge of the heating battery, it is possible to create voids in front of the heat exchangers, which increases the efficiency of storing thermal energy.

It should be taken into account that the orientation of the magnetic moments in the direction of the applied field is impeded by thermal motion. Taking into account both factors, as in the classical theory of paramagnetism of Langevin, leads to a formula for the magnetization of a magnetic fluid:

$$M = M_0 L\left(\frac{mH}{kT}\right) \tag{1}$$

$$M_0 = nm = \varphi M_s, L(\xi) = \mathrm{cth}\xi - \xi^{-1} \tag{2}$$

Because of the large magnitude of the moment m, the nonlinear effects appear quite early: the value of ξ 1 is reached at room temperature even in fields H ~ 102. If in conventional suspensions the gradients of the particle concentration are due solely to Archimedean forces, then for magnetic suspensions placed in an inhomogeneous field H , a gradient of the magnetic field plays a role analogous to the gravitational field. In an inhomogeneous field, the force (m) H acts on a particle with a magnetic moment m. Estimating the magnitude of this force, it should be borne in mind that for those particle sizes (d ~ 100 A), which are used in stable magnetic colloids, each suspended particle is separate magnetic domain. Calculating the critical dimensions below which the particle becomes absolutely single-domain leads to values of d from several hundred angstroms (330 and 760 A for iron and nickel, respectively).

4. Conclusions

1. The mechanisms of heat exchange in magnetic fluids based on synthetic oil containing ferromagnetic particles (nickel-zinc ferritic), paraffin and multilayered carbon nanotubes are studied.
2. A technique for experimental studies for a magnetic fluid based on synthetic oil containing ferromagnetic particles (nickel-zinc ferrite), paraffin and MWNTs has been developed. The range of measurements of the temperature field was from 20 to 75 ° C.
3. Experimental investigations of the temperature field of a magnetic fluid under various temperature conditions under the influence of a magnetic field produced by neodymium magnets with a magnetic induction of 1500 mT, as well as their analysis.

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