Lubricants with nanocarbon additives

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It is known that antiwear properties of engine oil depend on chemical composition and polarity of base oil, nature of additives and viscosity-temperature characteristics of the resulting oil. Since both deterioration of engines components and different friction regimes are determined by a huge number of factors, it is important to optimize antiwear properties of engine oils. The different wear nodes of an engine also require special optimization of the oil.

The number of publications on tribological properties of fullerenes and nanotubes is quite limited. Nevertheless, the existing data on mechanical strength, low surface energy, weak intermolecular interactions, etc. allow to draw a conclusion that the fullerenes and nanotubes are promising materials for various tribological tasks.

In this work we study the possibility of using nanocarbons as ashless additives for engine oils. The additives were prepared by compounding base oil with stabilizer and nanocarbon. Either fullerenes C_{60} or fullerene soot or carbon nanotubes were used as nanocarbon components of the additives. The concentration of carbon material in the samples varied in the range from 0.03 to 1 weight %. Lubricating additive C5-A or Borine alkali additive with antioxidant properties were used as stabilizers. Additional stabilization procedure was done for the compounded material by ultrasonic pulse processing.

Laboratory tests of the prepared carbon-containing samples of lubricants were carried out in a four-sphere friction machine (FSFM). The FSFM technique allows to measure the following tribological characteristics: score index, the critical load, the welding load and the diameter of wear spots.

The results of the tests showed that strong dependence of the tribological properties on the type and concentration of carbon material. This observation along with the revealed dependence on a compounding technique suggests that a nanocarbon-based superior lubricant composition is achievable.

Creation of nanocarbons with metal nanoparticles from GIC for different applications in catalysis

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Supported metals are widely used for catalytic applications; their activity is greatly improved when they are homogeneously scattered on a convenient support. Usually, they are prepared by an impregnation method, and the size of the particles and their distribution is relatively heterogeneous. Graphite is one of the convenient matrixes for different species intercalation and preparing fine metal particles homogeneously distributed on support. Graphite has a unique capability to form so-called graphite intercalation compounds (GICs), because of its layered structure. Molecules of intercalated species fill interlayer spaces and form monomolecular layers during intercalation process

Graphite with coin-shape metal clusters between adjacent graphene layers usually obtained after reduction of GICs. Unfortunately, this material has some disadvantages in utilizing. One of them is that only particles located on the lateral face of metal cluster are active because upper and bottom verges are covered by graphene sheets. In present work new approach base on simultaneous low temperature exfoliation and reduction of GICs was examined. This approach let us synthesize material represent thermal expanded graphite with supported metal clusters. Owing to not high exfoliation temperature (150-200°C) of new GICs, synthesized during the work, metal clusters didn't aggregate strongly and metal nanosized particles were obtained.

First time two original techniques: electrochemical oxidation and substitution intercalation, ? were utilized for production of graphite intercalation compounds (GICs) with hexachlorplatinic acid. Ternary H_2PtCl_6 - HNO_3 - GIC were synthesized by incomplete change reaction between the host HNO_3 – GIC (NG) with hexachlorplatinic acid. In all cases, irrespective of precursor GIC number, stage-2 GIC (Ic = 12.55? -12.60?) with H_2PtCl_6 formation was observed. Electrochemical oxidation of graphite in H_2PtCl_6 solution yields stage-2 H_2PtCl_6-GIC - graphite mixture and didn't let us synthesize single-phase product. Structure and properties of obtained samples was examined by number of methods: XRD, SEM, DSC, TG coupled with FTIR, XANES-EXAFS.

Later process of GICs reduction was investigated and optimal conditions such as temperature program, time of reduction, type of reducing agent was determined. Thus new type of nanosized material that show promise for catalyst applications was produced.

Application nanomaterials and nanotechnology plasmas for Lithium - Ionic Batteries with improved performance.

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The comparative tests of various materials for electrodes of Lithium-Ionic Accumulators have been carried out: the modified natural and synthetic graphite by the leading manufacturers (Superior Graphite, USA, and Nippon Carbon, Japan) and domestic material - carbon multiwall nanotubes (MWNT) and carbon single wall nanotubes (CSWNT).

Now the problem of use of lithium as a material of a negative electrode is solved for the account so-called "connections of introduction", or «intercalates". In such connections atoms of an ion of lithium take root into a crystal lattice of substance, settling down between it's units. However in these substances at intercalation - denticulation ions of lithium significant volumetric effects are observed. Only various forms of carbon have shown comprehensible sizes of volumetric effects.

Features of a crystal lattice of graphite allow achieving maximal ratio Li: C = 1:6, i.e. the structure intercalation corresponds to formula LiC_6. It corresponds to theoretical specific capacity of graphite 372 mAh/g. The best grades of graphite for lithium - ionic accumulators of conducting global firms Superior Graphite (USA), Nippon Carbon (Japan) have the specific electric capacity close to theoretical.

But the given size of specific capacity on the order of below theoretical specific capacity of metal lithium (3840 mAh/g).

It has caused intensive searches of the new materials, allowing increasing specific capacity of an electrode material.

By us it is established, that electrodes show specific capacity up to 1500 mAh/g-2100 mAh/g. on the basis of carbon nanomaterial - carbon nanotubes, received with plasmas nanotechnology.

In these Carbon MWNT and SWNT lithium at intercalation settles down not only between planes of a crystal lattice, but as it is supposed, and in nanohole. It is caused by structure and properties carbon MWNT which turn out in result use plasma nanotechnology.

It has been shown that application carbon nanotubes and plasmas nanotechnology allows to increase the specific capacity of lithium - ionic battery by 70-90% and more.

Fullerenes in magnetic materials

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Two ways of doping of Ñ-60 fullerenes in rapidly solidified Nd-Fe-B magnetic powders are investigated: a mechanoactivation and a homogenizing. The technology of vacuum capsulation of magnetic powders by fullerenes from a toluene solution is developed. Mechanoactivation process is carried out in a ball mill with speed of rotation up to 1500 rev/min and impact energy up to 15.000 W/kg. The homogenizing of powders is carried out in vacuum at temperature 700-900K. A structurally-phase condition of samples is investigated by means of methods X-ray and Mossbauer spectroscopy. Magnetic properties of samples are investigated by VSM with an induction up to 2.7 T.

It is shown that during a mechanoactivation the presence of 0.3-1.0 wt.% of fullerenes changes a structurally-phase condition of a rapidly solidified powder: the quantity of soft magnetic phases α-Fe decreases from 48 up to 25 vol.%; the average size of crystallites of phase decreases from 9 up to 5 nanometers; the NdO maintenance decreases from 4 up to 1 vol.%.

During a process of homogenizing the additive of 1.0 wt.% of fullerenes leads to reduction of the average size of $Nd_2Fe_{14}B$ phase crystallites and the optimum temperature of crystallization annealing decreases from 1000 up to 960K.

Influence of fullerenes on a mechanical strength of bonded magnets made on the basis of rapidly solidified powders is investigated. Introduction of 0.2 wt.% of fullerenes increases a mechanical strength of bonded magnets on 20-25%. The further increase in the maintenance of fullerenes leads to falling of a mechanical strength of bonded magnets. It can be caused by the fact that at 0.2 wt.% of fullerenes all particles of a magnetic powder are covered by a monolayer from molecules of fullerenes. An excess of this concentration of molecules of fullerene leads to formation of the second, the third, etc. layers around of particles of a magnetic powder. As molecular bonds between layers of fullerenes rather weak it leads to falling of a mechanical strength of a bonded magnet as a whole.

In bonded magnets made on the basis of HDDR-powders the mechanical strength practically does not change at doping of fullerenes up to 0.5 wt.%.

Difference in behavior of bonded magnets on the basis of rapidly solidified and HDDR-powders can be caused by different morphology of a surface of particles of these powders: the surface of particles of HDDR-powder is characterized by a greater roughness; therefore a lot of fullerenes for creation of a monolayer on a surface of a particle are required.

The development of technologies for nanomodified concrete production

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At the present stage of development of the building industry the materials with special properties (durability, rubbing resistance, protection against various kinds of penetrating radiations) are required. Alongside with traditional methods of problem solution rather perspective is the use of nanocarbon structures (carbon nanotubes and fullerenes) for the directed structurization of building composites. Concrete represents complex nanoleveled structure including hydrate phases of cement with the size of particles 1-100 nm, grains of initial cement (10-100 nm), additives and fillers. [1].

The suggested technology of nanomodified concrete production provides the usage of carbon nanomaterial (CNM) “Taunit” produced on the industrial reactor with productivity of 1500-2000 kg\year in TSTU. This material represents multilayered nanotubes with diameter of 20-40 nm and length up to 2 microns and more.

Within the framework of performance of the given project the following tasks were solved:

Selection of the optimum structure and ratio of fillers;

Selection of optimum modifier volume ;

Maintenance of even CNM distribution by various physicomechanical methods of influence (ultrasounds, variable electromagnetic field) in the water environment.

Preliminary experiments have shown, that samples of the modified fine-grained concrete have better bending performance. The gain of bending durability is about 20-30% and on compression durability - 15-20% in comparison with control samples with CNM volume of 0.022-0.0022% from total amount of the mixture.

The results were approved in laboratory of the factory FCP “Vodstroi” (Tambov). The increase of speed of durability growth in the experimental samples of concrete of mark of M 300 was established to be 50-70% in 7-day's term. On the 28-day's age samples had durability of 20% above the durabilities of control samples.

[1] B. Middendorf, N.B. Singh, *Cement International.* **4**, 80-86 (2006).

Tribology of fluoroplastics modified with fullerene soot

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Materials based on F-4 grade polytetrafluoroethylene containing various concentrations of carbon powder fillers possess high antifriction properties and decreased wear. For support surfaces of tribotechnical systems operating in water the mostly preferred filler is coke. F-4K20 composite, which is in widest use, contains 80% F-4 and 20% coke. The main drawback of F-4K20 is rather high friction coefficient (a factor of 2-3 higher than F-4).

The objective of this work was to prepare and study an antifriction polymers material (APM) combining low coefficient friction of F-4 and high resistance to wear of F-4K20.

We studied the effect of fullerene soot additives (initial soot produced in plasma electric discharge and soot remaining after fullerenes have been extracted with toluene from the initial soot (fullerene black)) on antifriction and antiwear properties of fluoroplastics F-4 and F-4K20 for sliding friction against steel with water lubrication.

Tests on samples of fluoroplastics F-4 and F-4K20 have shown that addition of 1% of either fullerene soot to F-4 results in significant increase in resistance to wear for water lubrication (to values exceeding those of F-4K20), with simultaneous decrease of the friction coefficient. For contact pressures in a range of 1–14 MPa the friction coefficient f and linear wear rate I_h decreased by a factor of 2–3.

For friction against steel with water lubrication addition to F-4 and F-4K20 of 1% fullerene black resulted in an increase of admissible operating pressures in tribology contacts by 25 and 20%, respectively.

Positive effect of fullerene soot additives on antifriction and antiwear properties of PTFE-based plastics makes them good candidates as APMs in sliding friction units against steel operating both without lubrication [1] and with water lubrication.

[1] B.M. Ginzburg, D.G. Tochil'nikov, A.A. Shepelevskiy, A.M.Leksovskiy, Sh. Tujchiev. *Zhurnal Priklad. Khimii* **79**,1534 (2006).

Structure and transport properties of fullerene – polyamide membranes

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Novel membranes with high permeability and selectivity are required for membrane technologies that are widely applied in industrial and ecological processes. Polymer modification is a mean for improving specific properties of the membrane material. In the present work poly(*m*-phenyleneisophtalamide) (PA) was modified by fullerene C_{60} incorporation. The aim of the work was formation of asymmetric membranes based on C_{60}-PA compositions and study on their structure and transport properties. To estimate the fullerene C_{60} effect on PA membrane properties, the similar membranes based on PA modified by other nanocarbon additives such as soot and nanotubes were prepared and studied. Compositions of PA with fullerene or other nanocarbon additives (soot and nanotubes Astralene®) were prepared by solid-phase interaction and used for asymmetric porous membranes formation. The membranes morphology was investigated by scanning electron microscopy.

PA modification by fullerene C_{60} up to 10 wt.% leads to change some parameters of asymmetric membranes: decrease of overall porosity, decrease of water flux through membranes, and increase in contact angle of water on membrane surface. C_{60}-PA membranes were compared with PA membranes modified by 5 wt.% other nanocarbon additives (soot and nanotubes) in filtration of water, ethanol, hexane, and isopropanol. The membrane permeability depends on the nature of additives and increases in the following order: nanotubes < fullerene < pure PA < soot. PA membranes modified by 5 wt.% different nanocarbons were submitted to the ultrafiltration test using aqueous solution of protein mixture. Flux of aqueous protein mixture was lower than water flux for all membranes. One possible reason for the decreasing flux is protein sorption on surface and into pores of membranes. This suggestion was tested in dynamic (filtration) and static (sorption) experiments. By this way, it was established that properties of PA membranes modified by fullerene and nanotubes differ markedly from the pure PA membranes. Soot acts as a mechanical dopant to PA, does not change rejection, and slightly increases flux.

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Semi-empirical researches of sensor properties of carbon nanotubes with boundary functionalisation

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The opportunity of open tubulen border by heteroatoms and functional groups provides the opportunities of reception of new structures on the basis of carbon nanotubes. The calculations of carbon tubes with boundary functional groups are executed for nanotubes (6, 0) within the model of molecular cluster using semi-empiric scheme MNDO [1]. The analysis of the electronic structure of nanotubes, closed by chosen functional groups O, OH, and NH_2 has installed the basic contributions of nuclear orbits of modifying atoms in a conductivity zone and valent zone of the turning out systems. Features of geometrical structure of tubes, modified by functional groups are revealed, character of groups symmetry concerning an tube's axis is analysed.

Absolutely new opportunities opens while using chemically modified nanotubes with specially chosen functional groups on the border of tubes. In this case it manages to investigate not only a relief of a surface of the investigated sample, but also the chemical compound of the surface. It determines an opportunity to use way the similar modified tubes as a sensor for defining the chemical elements of the various nature. We had investigated the nanotube which the open end was isolated by carboxyl (-ÑÎ Î Í) group. As a cluster models have been chosen the fragment of tube containing 72 atoms of carbon. Features of spatial orientation of carboxyl groups rather nanotubes and its geometrical parameters have been revealed. It has appeared, -COOH the group joins to nanotube under a corner 30. Calculations of interaction of the probe constructed this way on the basis of tube with atom Na are executed. Process of scanning of an any surface was modelled and activity of functional group concerning the chosen atom of alkaline metal was defined. The analysis of the power curve of interaction constructed as a result of calculations has established, that nanotube with specially chosen chemical group, becomes chemically sensitive concerning atomic Na. It is proved the opportunity of using modified carbon nanotubes as a sensor controls on the certain elements and radicals.

[1] I.V. Zaporotskova, N.G. Lebedev, P.A. Zaporotskov, Abstracts of International Conference “Fullerenes and Atomic Clusters” June 27 – July 1, 2005, St.-Peterburg, p. 314.