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TRIBOLOGICAL CHARACTERISTICS OF THE DIAMOND-LIKE CARBON FILMS COVERED BY HYDROGEN OR FLUORINE*: AB INITIO* CALCULATIONS

Within the methods of electron density functional and ab initio pseudopotential, it were obtained the spatial distributions of density of valence, the total energy, the static friction force for diamond and diamond-like films with uncoated surfaces or covered completely with hydrogen, or with a half coating hydrogen or fluorine. It was found that the half concentration of the broken bonds of carbon atoms on the smooth surfaces of diamond films, which exist in tribological contact, increases the slip resistance by comparison with the films with surface complete covered by hydrogen.

Keywords: the electron density functional method, the pseudopotential method, the diamond-like carbon, adhesion, the static friction force, hydrogen, fluorine.

Introduction and statement of the problem

Tribology is the science of friction, wear and lubrication material - is an important, given its numerous technological applications. Processes of friction, wear and lubrication of new composite materials, which are currently replace protective metal surface coatings, significantly different from the processes characteristic of metals [1], hence, the understanding of tribology of nonmetals is important. Knowledge about tribology at the atomic level can be obtained on a theoretical basis by means of the molecular dynamics and the quantum chemical calculations.

In this paper, we performed the first principles simulation of tribology processes. The essence of this simulation is based on the static energy calculations. Calculation algorithm consisted in the following.

The initial structure of model objects was generated like that; the pair of friction surfaces were aligned in the desired configuration and installed at a short distance of separation D (Fig.1). The energy of such a structure was calculated and stored. Then, the surface atomic layers moved on short distance relatively the deeper atomic layers, in the time of the distance of separation (D) was unchanged, and new energy was calculated.

This procedure repeated again, thereby the energy relief along the trajectory of the shift of atomic layers was generating. Calculated energy relief allows estimating the normal pressure and friction coefficient. The friction coefficient is a measure of the work, which was conducted in the system, is transformed into other less-managed forms of energy. Clearly, there is a significant correlation between the adhesion, the friction and the wear of surfaces, which slide over each other, and the details of the correlations depend on the specifics of their atomic structure.

Diamond-like carbon (DLC) has recently attracted considerable attention as a semiconductor lubricant. The high content of the carbon atoms with diamond bonds in the presence of similar graphite bonds leads to the appearance of the unique characteristics of diamond-like coatings, such as wear resistance, high strength, chemical resistance, low friction, poor abrasion, biocompatibility, transparency in the infrared range of the spectrum and ecological purity [2]. Some factors, such as surface atoms in the DLC and structure of the film are essential to improve tribological characteristics of DLC [3].

Models and methods of calculation

In these computing experiments, we investigated the influence of the roughness and the dangling bonds of the slipping surfaces on the value of adhesion and friction coefficient using its own software complex [4].

All of our evaluations of the static structural properties through the evolution of energy are based on the following assumptions. (1) The electrons are in the ground state in relation to the instant positions of nucleases (adiabatic approximation of the Born-Oppenheimer). (2) The multiparticle effects are assessed in the framework of the local density functional formalism. (3) There is used approximation of frozen cores that is pseudopotential. Pseudopotential theory gives the possibility to use convenient mathematical Fourier functions. Through a pseudopotential weakness as a basis in expanding the single-particle electron wave functions possible applicants the plane waves. Relying on artificial translational symmetry objects, which we explore the expression for the total energy simply is formulated in the momentum space. The total

$$\begin{aligned}E_{tot}/\Omega = &\sum_{k,G,i}\left|\Psi_i(\vec{k}+\vec{G})\right|^2 \frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2 + \\ &+\frac{1}{2}4\pi e^2 {\sum_G}' \frac{\left|\rho(\vec{G})\right|^2}{\vec{G}^2} + \sum_G \varepsilon_{xc}(\vec{G})\rho^*(\vec{G}) + \\ &+ {\sum_{G,\tau}}' S_\tau(\vec{G}) V_\tau^L(\vec{G})\rho^*(\vec{G}) + \\ &\sum_{k,G,G',i,l,\tau} S_\tau(\vec{G}-\vec{G}')\Delta V_{l,\tau}^{NL}(\vec{k}+\vec{G},\vec{k}+\vec{G}')\times \\ &\times\Psi_i(\vec{k}+\vec{G})\Psi^*{}_i(\vec{k}+\vec{G}') + \\ &+\left\{\sum_\tau \alpha_\tau\right\}\left[\Omega^{-1}\sum_\tau Z_\tau\right] + \Omega^{-1}\gamma_{Ewald},\end{aligned} \quad ,(1)$$

where $\vec{k}$ is the value from the first Brillouin zone, $\vec{G}$ - vector of the reciprocal lattice, $\Psi_i(\vec{k}+\vec{G})$ - the single-particle electron wave function, *i* - denotes the occupied states for a specific $\vec{k}$, $\rho(\vec{G})$ - coefficient in expanding the valence electrons density, ∑' – primes in the summation exclude $\vec{G}$=0 term, $\vec{\tau}$ - the number of atoms in the unit cell, $S_\tau(\vec{G})$ is a structural factor, V_τ^L is the local (l-independent) spherically symmetric pseudopotential, 1 denotes the orbital quantum number, $\Delta V_{l,\tau}^{NL}$ - a nonlocal (1-dependent) additive V_τ^L, Z_τ - charge of an ion, γ_{Ewald} - it is the energy of Madelung of the point ions in a uniform negative background.

The coefficients of the Fourier transformation of the electron charge density are calculated by the formula:

$$\rho(\vec{G}) = \sum_i \sum_{\vec{G}',\alpha} \Psi_i(\vec{k}+\vec{G})\Psi^*{}_i(\vec{k}+\alpha\vec{G}'), \qquad (2)$$

where $\Psi_i(\vec{k}+\vec{G})$ - the coefficients in expending the single-particle electron wave functions over the plane wave are obtained from the zone-structural calculations, α – the operator symmetric transformations from the point group symmetry of the unit cell.

To calculate the electron exchange-correlation energy ε_{xc}, we used the Ceperley-Alder approximation with the Perdew-Zunger parameterization.

The $\vec{k}$ integration was replaced by a discrete summation over the special points the Brillouin zone.

The tribological contact model created from the diamond-like films by each thickness of about 7 Å. In films the percentage of the graphite-like bonds changed from zero (see Fig.1) to 50 (see Fig.2). The percentage part changed the smoothness of surfaces.

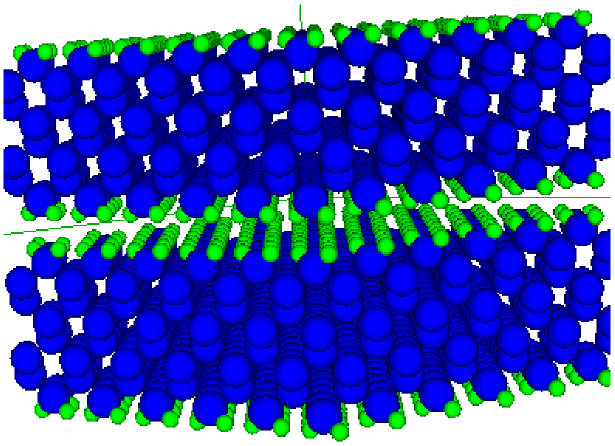


Fig.1. The (100) surface of the diamond-like carbon films with the surface hydrogen atoms and 100% diamond-like bonds in tribological contact.

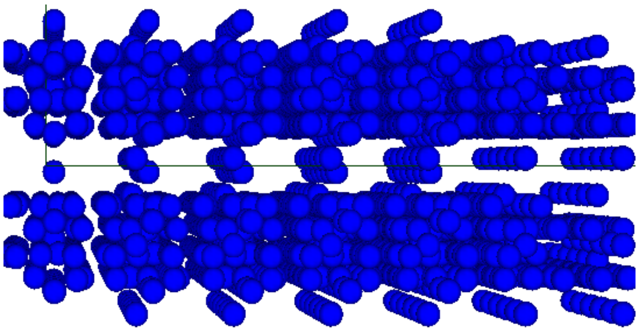


Fig. 2. Two diamond-like carbon films with a mixture of 50% the diamond-like and 50% the graphite-like bonds in tribological contact.

In connection with that, the algorithm of calculation expects presence of translational symmetry in the probed atomic system, the artificial superlattice of orthorhombic type was at first created. The object of study defines the super lattice parameters and the atomic basis. Therefore, the atomic basis of the primitive cell of the artificial super lattice for simulation of two diamond-like carbon films with a mixture of 50% the diamond-like and 50% the graphite-like bonds in tribological contact consisted from 88 the carbon atoms. Translation operations of the described cells resulted to the two infinite films. They were paralleled axis Z and located at a certain distance D from each other (Fig. 2, Fig. 6). We calculated the total energy of objects in tribological contact and theirs spatial distribution of the valence electrons density.

The calculation results and theirs discussion

On Fig.3 and Fig.4 there are changes of the total energy and the rate of the total energy change of two the diamond-like carbon films with a mixture of 50% the diamond-like and 50% the graphite-like bonds versus the change of the separation distance between films D (the value of the derivative dE/dD is considered to be the friction force).

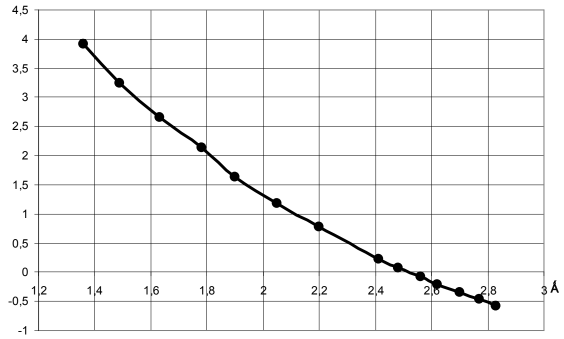


Fig. 3. The changes of the total energy of two diamond-like carbon films with a mixture of 50% the diamond-like and 50% the graphite-like bonds versus the change of the separation distance between films D. Energy is supplied in atomic units per atom, distance - in Å.

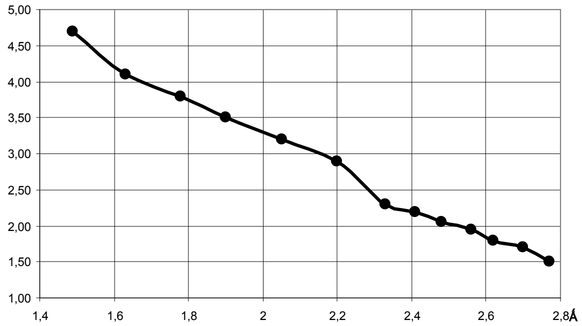


Fig.4. Friction force change (dE/dD) of two the diamond-like carbon films with a mixture of 50% the diamond-like and 50% the graphite-like bonds versus the change of the separation distance between films D.

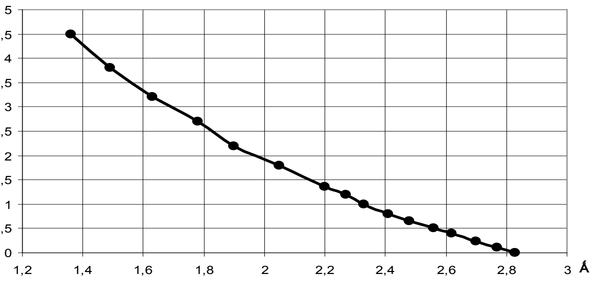
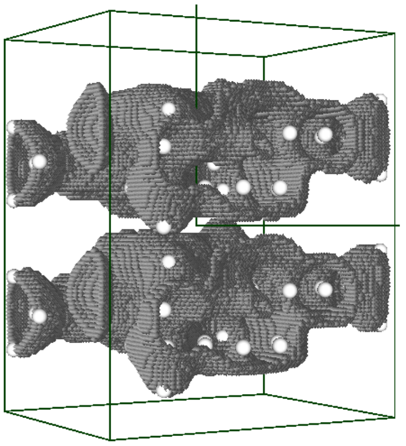


Fig. 5. The adhesion energy change (dE/dD) of two the diamond-like carbon films with a mixture of 50% the diamond-like and 50% the graphite-like bonds versus the change of the separation distance between films D. Energy is supplied in atomic units per atom, distance - in Å.

a



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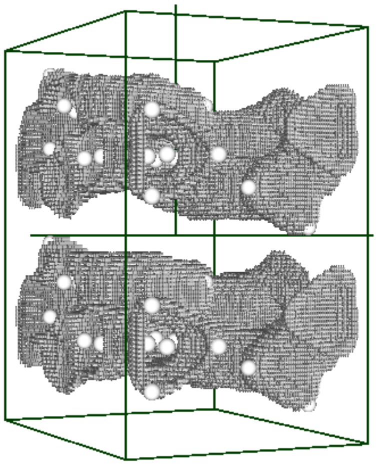
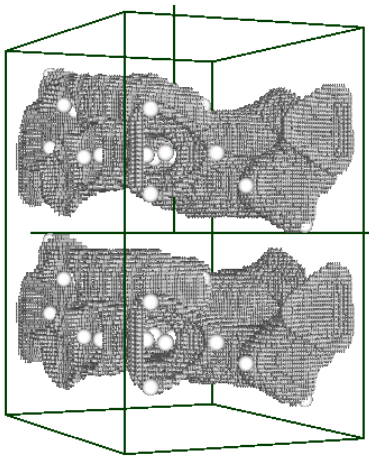




c

Fig. 6. The spatial distribution of the valence electrons density for value 0.1 from the maximum in two the diamond-like carbon tribological contacted films with a mixture 50% the diamond-like and 50% the graphite-like bonds, the separation distance D between the films is: a) 1.36 Å, b) 2.2 Å, c) 2,77 Å.

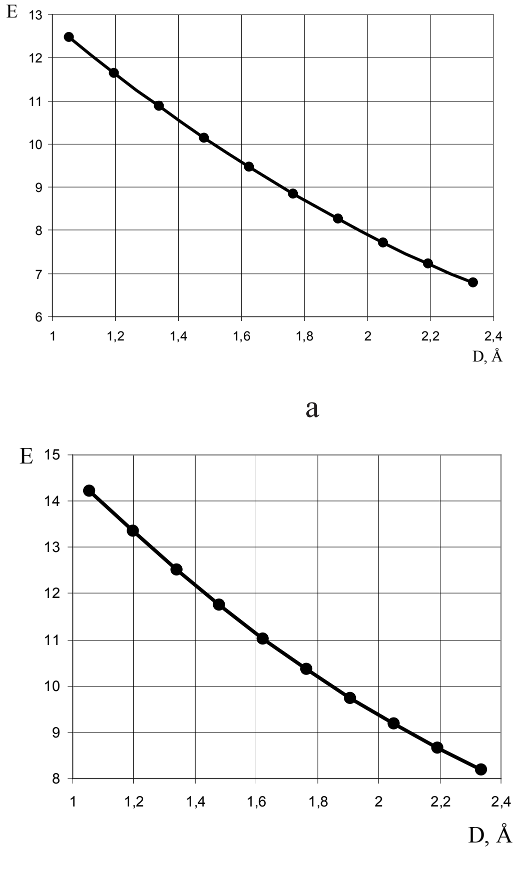
The graph in Fig.4 shows that for the separation distance (D) in the area of 2.2-2.3 Å on the (dE/dD) curve there is an inflection, which can be associated with changes in the nature of interaction between the films. Comparing this fact with the spatial distribution of the density of the valence electrons for different distances of separation (D) between films, we conclude that the electronic exchange between films disappears at these distances, i.e. the acceptor-donor type of interaction disappears. As to the more long Coulomb interactions between the carbon ions, then they disappear on distances close to 2.83 Å. About this the zero value of adhesion energy between the films in Fig.5 witnesses. The adhesion energy between the films was calculated as a difference between the total energy of the two isolated diamond-like films and the energy of the tribological contacted films.

Further, the atomic basis of the primitive cell of the artificial super lattice for simulation of two the diamond films by thickness of 7.5 Å with a complete coverage of hydrogen consisted of 48 atoms; and for simulation of the 50% coverage of hydrogen or fluorine consisted of 40 atoms. Translation operations of the described cells resulted to the two infinite films. They were paralleled axis Z and located at a certain distance

D from each other. For simulation of the elastic displacements (without destruction of chemical bonds) of the surface layers of the sliding films relatively the deeper layers at a constant distance between the films, the atomic layers of hydrogen and the nearest carbon are moved not more than 7% of the interatomic distances. We calculated the total energy objects in the tribological sliding contact, the static friction force, as a derivative ($\Delta E/\Delta l$), where ΔE is the energy change versus the displacement of the surface atoms on the Δl, and the spatial distribution of density of valence electrons.

On Fig.7 and Fig. 8, it shows the change of the total energy of two the diamond sliding films with a complete coverage of hydrogen and the 50% coverage of hydrogen or fluorine versus a change of the distance of separation D between films.

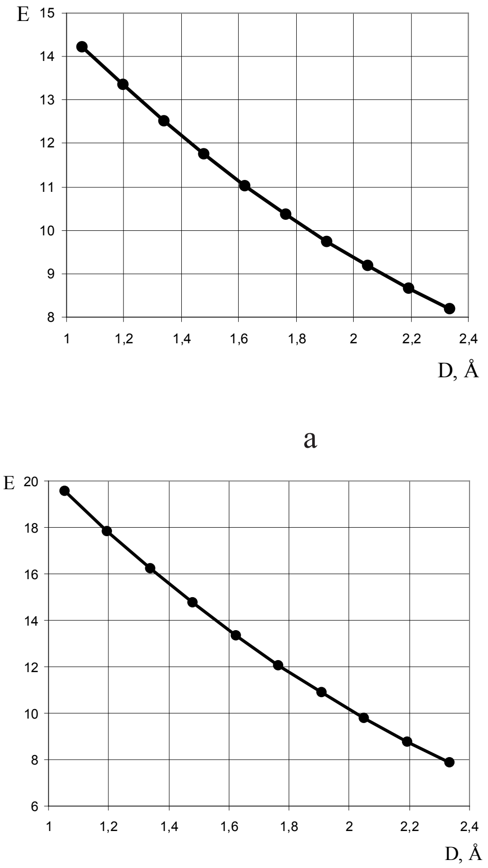
From Fig. 7 and Fig. 8, it shows that with increasing a separation distance between the diamond films, the total energy of the films with the fully hydrogen passivated surfaces and the 50% coated films by fluorine or hydrogen decrease monotonically. Herewith, on 14% greater energy in the close contact films (the separation distance D between the films was 1.197 Å) the film contacts with the incomplete hydrogen coverage has by comparison with the film contacts with the complete hydrogen coverage. In addition, on 37% greater energy the film contacts with the incomplete fluorine coverage has by comparison with the film contacts with the incomplete hydrogen coverage. When the films with the various surface coverage's are removed one from other to the distance D, equal 2.336 Å, the total energy of these systems had almost the same value.



a

b

Fig. 7. The change of the total energy of two the sliding diamond films with the full hydrogen coverage (a) and the 50% hydrogen coverage (b) at change of the separation distance D between films. Energy is supplied in atomic units per atom, distance - in Å.

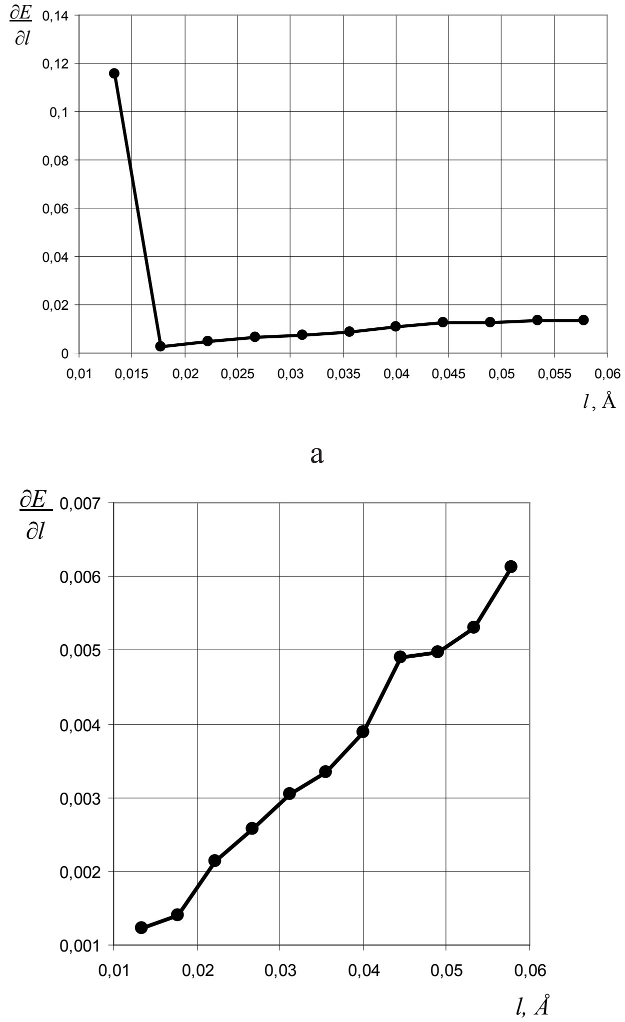


a

b

Fig. 8. The change of the total energy of two the sliding diamond films with the 50% hydrogen coverage (a) and the 50% fluorine coverage (b) at change of the separation distance D between films. Energy is supplied in atomic units per atom, distance - in Å.

At the fixed separation distances (D) between films (the most close contact, D=1.197 Å, the most remote contact, D=2.336 Å) the static friction forces in tribological contacts of two diamond films coated by 50% fluorine, or 50% hydrogen, or complete hydrogen coverage are examined. The dependencies of the calculated friction forces versus the displacement of the surface atomic layers are shown in Fig. 9, Fig. 10 and Fig. 11.

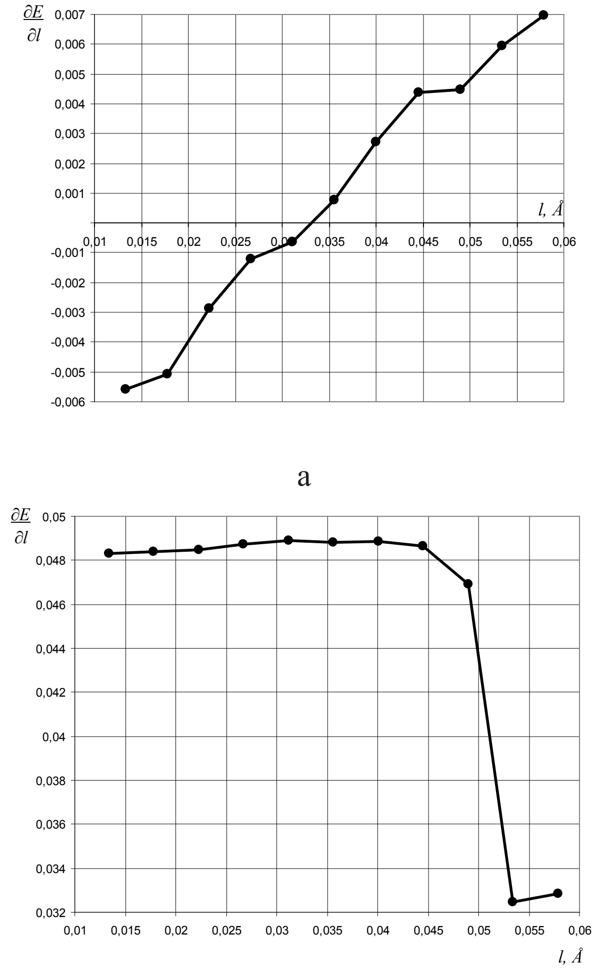


a

b

Fig. 9. The static friction force of two diamond films with full hydrogen coating, these films slid one comparatively other with the displacement of the surface atoms. The separation distances D between the films were: a) 1.197 Å, b) 2.336 Å.

From Fig. 9b and Fig. 10b it shows that the partial removal of hydrogen atoms from the surface of the film leads to the increase of the static friction force more in comparison with a complete hydrogen coverage of surfaces of diamond films in the most remote tribological contact. Incomplete fluorine covering of the films surfaces increases the coefficient of friction else on order of magnitude in comparison with hydrogen coatings (see Fig. 11).

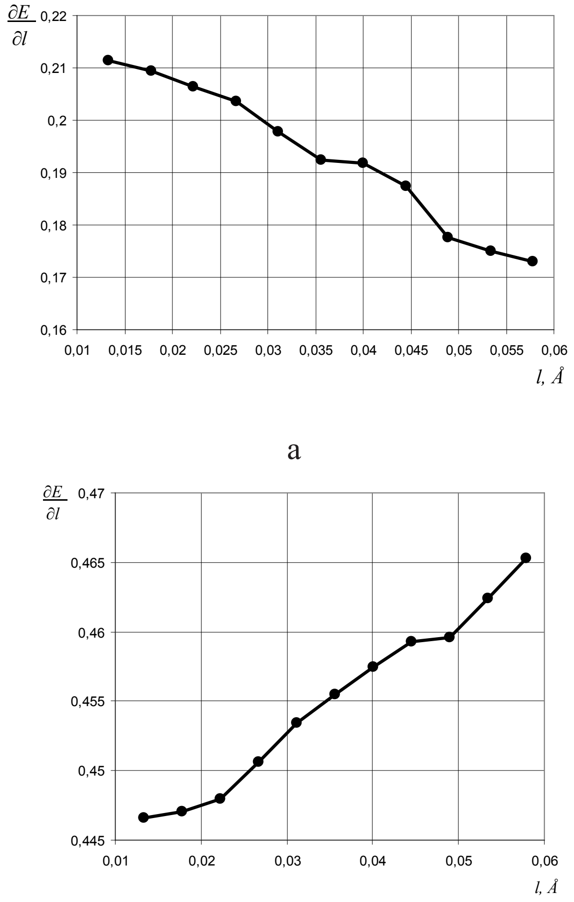


a

b

Fig. 10. The static friction force of two diamond films with 50% hydrogen coating, these films slid one comparatively other with the displacement of the surface atoms. The separation distances D between the films were: a) 1.197 Å, b) 2.336 Å.

Analyzing the static friction forces of two diamond films, which slid one comparatively other with the displacement of the surface atoms and were covered under different conditions (Fig. 9 - Fig. 11), we observe a non-monotonic fluctuations in the value of the static friction force in these systems. Almost all above discussed tribological contacts were characterized by increase a friction coefficient when the shift of the surface atomic layers comparatively more deep increase, except the diamond films coated by 50% fluorine, which were in the closest contact (see Fig. 11a).



a

b

Fig. 11. The static friction force of two diamond films with 50% fluorine coating, these films slid one comparatively other with the displacement of the surface atoms. The separation distances D between the films were: a) 1.197 Å, b) 2.336 Å.

Conclusions regarding the increase of the coefficient of friction, were installed and other researchers in considering the properties of carbon materials. Frictional properties of monocrystalline diamond surface (111) were studied in ultra-high vacuum (UHV) with the help of silicon (Si) needle the AFM. On the surface the presence or absence of hydrogen (H) being tracked by diffraction of slow electrons (LEED). Removal of the hydrogen from the surface leads to the increase of average coefficient of friction is more than two orders of magnitude compared with the surface covered with hydrogen. This is a vivid and convincing example of how loose connection can connect border and increase the influence of adhesion to friction, and how passivation those relations that react may significantly weaken these forces [5-10].

In Fig. 12 and Fig. 13 the spatial density distributions of valence electrons within the interval of 0.1–0.2 of the maximum value (this lowest value of density defines the limit of the films and determines their size and shape) in the diamond films with the different coverage of the surface are given. Herewith the separation distances D between the films changed from 1.054 Å to 2.336 Å with step 0.1424 Å. From these drawings it is clear that the type of the surface coating of the diamond film considerably influences upon the restructuring of the distribution of the valence electrons on the surface, and in the field of between films and in the inner layers of the films. As follows at the presence of the incomplete bonds of the surface carbon atoms in the spatial distribution of electrons the extracted from the surface regions are appeared.

In Fig. 14 the spatial density distributions of valence electrons within the interval of 0.3–0.4 of the maximum value in the diamond films with the 50% fluorine coverage of the surface are given. Herewith the separation distances D between the films changed from 1.054 Å to 2.336 Å with step 0.1424 Å.

On drawing Fig. 15 comparison of the spatial distributions of the valence electrons density in the tribological contact of two diamond films coated by 50% hydrogen or 50% fluorine are realized, these films were situated on distance of separation between films 1.197 Å and 2.336 Å.

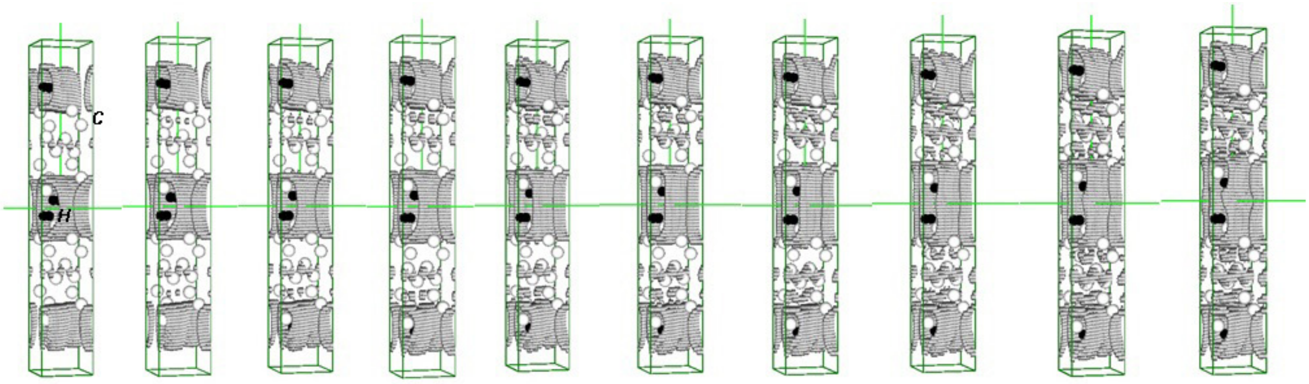


Fig. 12. The spatial distribution of the valence electrons density within the interval of 0.1–0.2 of the maximum value in the tribological contact of two diamond films with the complete hydrogen coverage for the separation distance D between films 1.054 Ǻ, 1.197 Ǻ, 1.339 Ǻ, 1.482 Ǻ, 1.624 Ǻ, 1.766 Ǻ, 1.909 Ǻ, 2.051 Ǻ, 2.194 Ǻ, 2.336 Ǻ (respectively from left to right).

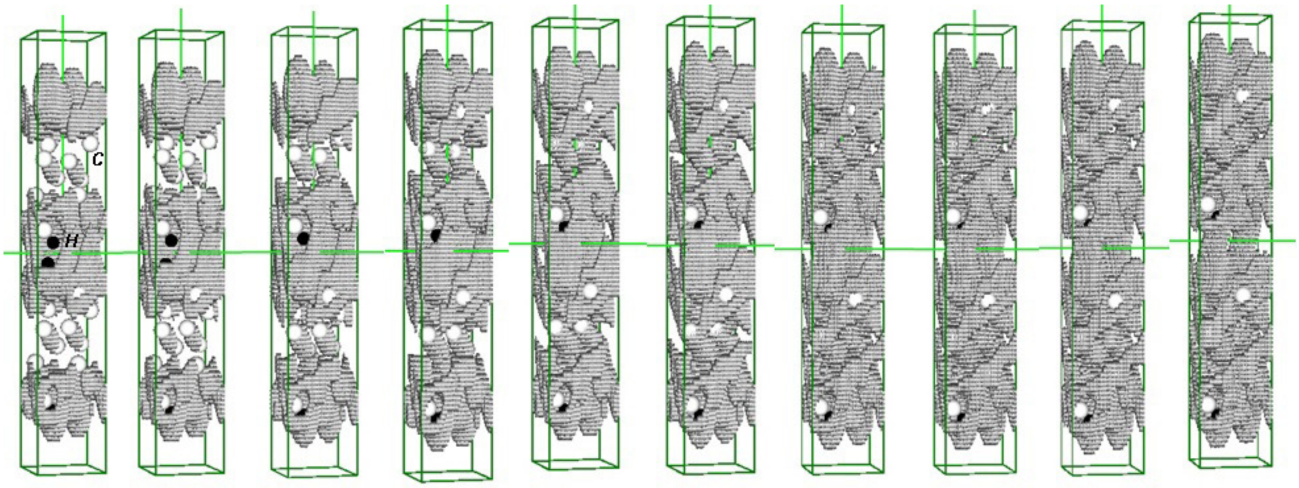


Fig. 13. The spatial distribution of the valence electrons density within the interval of 0.1–0.2 of the maximum value in the tribological contact of two diamond films with the incomplete (50%) hydrogen coverage for the separation distance D between films 1.054 Ǻ, 1.197 Ǻ, 1.339 Ǻ, 1.482 Ǻ, 1.624 Ǻ, 1.766 Ǻ, 1.909 Ǻ , 2.051 Ǻ, 2.194 Ǻ, 2.336 Ǻ (respectively from left to right).

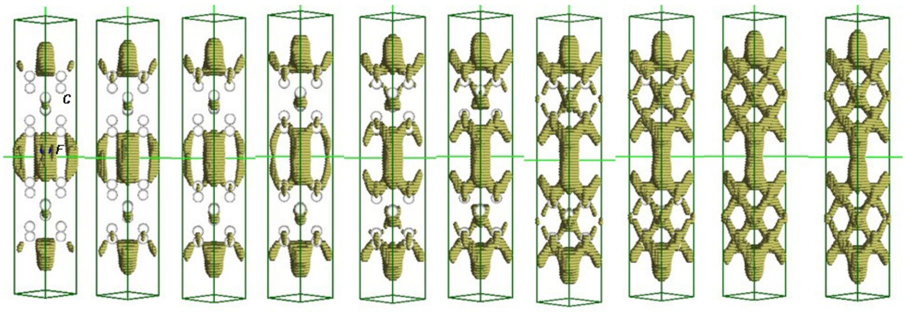
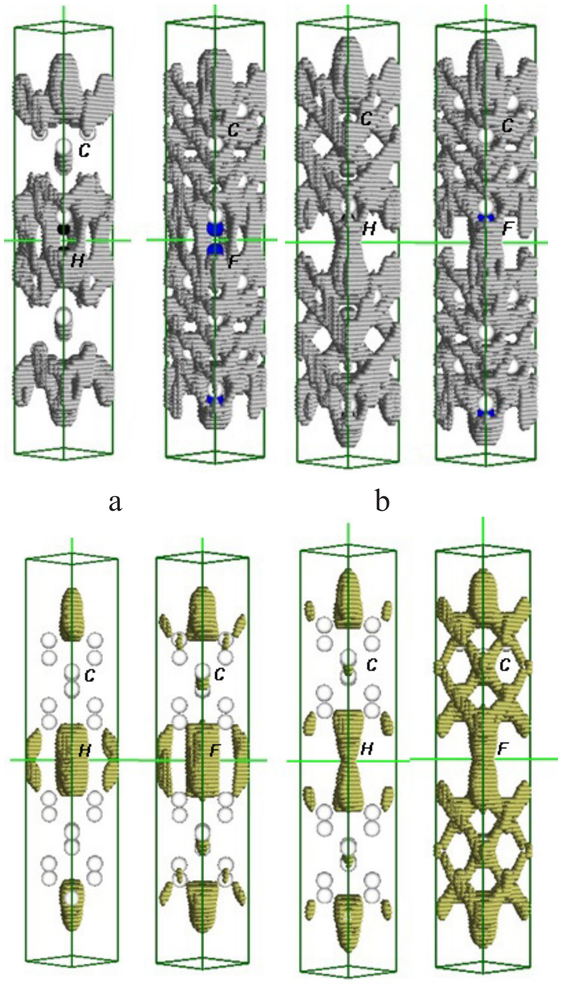


Fig. 14. The spatial distribution of the valence electrons density within the interval of 0.3–0.4 of the maximum value in the tribological contact of two diamond films with the incomplete (50%) fluorine coverage for the separation distance D between films 1.054 Ǻ, 1.197 Ǻ, 1.339 Ǻ, 1.482 Ǻ, 1.624 Ǻ, 1.766 Ǻ, 1.909 Ǻ , 2.051 Ǻ, 2.194 Ǻ, 2.336 Ǻ (respectively from left to right).



a b

c d

Fig.15. The spatial distribution of the valence electrons density within the interval of 0.1–0.2 of the maximum value and within the interval of 0.3–04 in the tribological contact of two diamond films coated by 50% hydrogen and 50% fluorine, respectively: a), c) the separation distance between the films is 1.197 Å; b), d) the separation distance between the films is 2.336 Å.

Comparing the valence electron density distributions for the two diamond sliding films coated by 50% hydrogen or 50% fluorine (Fig. 13-15), see the localization of electronic charge in the contact area between the films is present. This charge can be interpreted as static charging films that slip. The most brightly seen localization of its kind in tribological contacts of films coated by hydrogen is fixed when the separation distance D between the films is 1.197 Å.

Conclusions

The methods of electron density functional and pseudopotential theories were used to calculate the distributions of valence electron density, the total energy and static friction for diamond or diamond-like films with uncovered surfaces or covered by hydrogen or fluorine.

It is determined that the change in the friction force between two the slip rough diamond-like carbon films with thickness about 7 Å each and with a mixture of 50% diamond-like and 50% graphite-like bonds without coverage is due to the changing nature between atomic interaction from the short donor-acceptor to the long-range Coulomb.

It was found that the half concentration of the broken bonds of carbon atoms on the smooth surfaces of diamond films, which exist in tribological contact, increases the slip resistance by comparison with the films with surface complete covered by hydrogen. This increase occurs on magnitude of one order for the films coated by 50% hydrogen and on two orders for the films coated by 50% fluorine.

For diamond films coated by 50% fluorine or 50% hydrogen, which slithered one comparatively another with a shift of the surface atoms, a non-monotonic fluctuations in the value of static friction are characterized, i.e. the instability of their tribological properties is revealled.

For two diamond films coated by hydrogen or 50% fluorine, which exist in tribological contact, it is observed the areas of localization of electronic charge at the site of contact between the films, which were treated as static charging of films that slipped.

References

1. K. Holmberg, H. Ronkainen, A. Matthews. Tribology of thin coatings // Ceram. Int. – 2000. – Vol. 26. – P. 787–795.
2. K. Hayashi, K. Tezuka, N. Ozawa, T. Shimazaki, K. Adachi, and M. Kubo. Tribochemical Reaction Dynamics Simulation of Hydrogen on a Diamond-

Like Carbon Surface Based on Tight-Binding Quantum Chemical Molecular Dynamics // J. Phys. Chem. C, 115(46), pp. 22981-22986 (2013).

3. G. T. Gao , Paul T. Mikulski , Judith A. Harrison. Molecular-Scale Tribology of Amorphous Carbon Coatings: Effects of Film Thickness, Adhesion, and Long-Range Interactions // J. Am. Chem. Soc., 124 (24), pp 7202–7209 (2002).
4. R. M. Balabai, Ukrainian Journal of Physics 58, 389 (2013).
5. Researchers unstick nanoparticle friction // Nano Today, 2011, Volume 7, Issue 1, P. 2.
6. Raisa Neitola, Tapani A. Pakkanen. Ab Initio Studies on the Atomic-Scale Origin of Friction between Diamond (111) Surfaces // J. Phys. Chem. B, 2001, 105 (7), pp 1338–1343.
7. Guangtu Gao, Rachel J. Cannara , Robert W. Carpick , Judith A. Harrison. Atomic-Scale Friction on Diamond: A Comparison of Different Sliding Directions on (001) and (111) Surfaces Using MD and AFM // Langmuir, 2007, 23 (10), pp 5394–5405.
8. G. Zilibotti, M. C. Righi. Ab Initio Calculation of the Adhesion and Ideal Shear Strength of Planar Diamond Interfaces with Different Atomic Structure and Hydrogen Coverage // Langmuir, 2011, 27 (11), pp 6862–6867.
9. Maria-Isabel De Barros Bouchet, Giovanna Zilibotti, Christine Matta, Maria Clelia Righi, Lionel Vandenbulcke, Beatrice Vacher, Jean-Michel Martin. Friction of Diamond in the Presence of Water Vapor and Hydrogen Gas. Coupling Gas-Phase Lubrication and First-Principles Studies // J. Phys. Chem. C, 2012, 116 (12), pp 6966–6972.
10. Shandan Bai, Tasuku Onodera, Ryo Nagumo, Ryuji Miura, Ai Suzuki, Hideyuki Tsuboi, Nozomu Hatakeyama, Hiromitsu Takaba, Momoji Kubo, Akira Miyamoto. Friction Reduction Mechanism of Hydrogen- and Fluorine-Terminated Diamond-Like Carbon Films Investigated by Molecular Dynamics and Quantum Chemical Calculation // J. Phys. Chem. C, 2012, 116 (23), p. 12559.

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Abstract

It was found that the half concentration of the broken bonds of carbon atoms on the smooth surfaces of diamond films, which exist in tribological contact, increases the slip resistance by comparison with the films with surface complete covered by hydrogen. This increase occurs on magnitude of one order for the films coated by 50% hydrogen and on two orders for the films coated by 50% fluorine.

For two diamond films coated by hydrogen or 50% fluorine, which exist in tribological contact, it is observed the areas of localization of electronic charge at the site of contact between the films, which were treated as static charging of films that slipped

Key words: tribological contact, the concentration, the diamond-like carbon, hydrogen, fluorine

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ТРИБОЛОГІЧНІ ХАРАКТЕРИСТИКИ АЛМАЗОПОДІБНИХ ВУГЛЕЦЕВИХ ПЛІВОК, ПОКРИТИХ ВОДНЕМ АБО ФТОРОМ: РОЗРАХУНКИ AB INITIO

Резюме

Було встановлено, що половинна концентрація незавершених зв'язків атомів вуглецю на гладких поверхнях алмазних плівок, що у трибологічному контакті, збільшує опір ковзанню у порівнянні з плівками з повністю завершеними воднем поверхнями: на порядок для плівок, покритих на 50% воднем, і на два порядки для плівок, покритих на 50% фтором.

Для двох алмазних плівок з покриттям воднем чи фтором у 50% у трибологічному контакті спостерігалися області локалізації електронного заряду в місці контакту між плівками, котрі трактувалися як статичне зарядження плівок, що ковзали.

Ключові слова: трибологічний контакт, концентрація, алмазоподібні вуглецеві плівки, водень, фтор.

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ТРИБОЛОГИЧЕСКИЕ ХАРАКТЕРИСТИКИ АЛМАЗОПОДОБНЫХ УГЛЕРОДНЫХ ПЛЕНОК, ПОКРЫТЫХ ВОДОРОДОМ ИЛИ ФТОРОМ: РАСЧЕТЫ AB INITIO

Резюме

Было установлено, что половинная концентрация незавершенных связей атомов углерода на гладких поверхностях алмазных пленок, в трибологическом контакте, увеличивает сопротивление скольжению по сравнению с пленками с полностью завершенными водородом поверхностями: на порядок для пленок, покрытых на 50% водородом, и на два порядка для пленок, покрытых на 50% фтором.

Для двух алмазных пленок с покрытием водородом или фтором в 50% в трибологическом контакте наблюдались области локализации электронного заряда в месте контакта между пленками, которые трактовались как статический заряд пленок, которые скользили.

Ключевые слова: трибологический контакт, концентрация, алмазоподобные углеродные плёнки, водород, фтор.