

# QUANTUM-CHEMICAL RESEARCH of BORON and OXYGEN HETEROATOMS INFLUENCE on CARBON MATERIALS STABILITY

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## Introduction

Boron-containing carbon materials are actively investigated due to their oxidizing stability and high efficiency to intercalation of Li atoms in using these materials as anodic Li-batteries masses, in creation of supercapacitors and also unique systems generating and savings energy [1-4].

Earlier [5,6] one of the authors has discussed three possible mechanisms of the influence of boron additives in carbon materials on increase of their thermooxidizing stability. So, it was assumed, that boron, due to its less electron amount, than in carbon atom can work in carbon matrix as electron-acceptor, which presence lowers Fermi level of this carbon material. The second mechanism of oxidizing ability inhibition was associated with more high order of graphite-similar structure at the presence of boron atom in a molecular skeleton of carbon material. At last, the third possible mechanism assumes formation on carbon surface the glass-similar  $B_2O_3$ , which prevents the access of oxygen to a carbon surface and works as a physical barrier.

It is necessary, truth to note, that as a result of researches executed by the authors [7,8], the first two mechanisms of boron inhibition influence on oxidizing stability of carbon materials should be recognized as the most probable mechanisms, though at large boron concentration in carbon matrix the opportunity of the third mechanism is not excluded also [9].

Taking into account, that the oxidizing processes are caused by electron density transfer from carbon matrix on a particle which is oxidized (oxygen molecule, other reacting molecule or cation), one of the most probable mechanisms of boron inhibiting action on thermooxidative processes in carbon materials can be connected to influence of boron atoms on electron-donor ability of B-containing carbons, i.e. on energy levels of the highest occupied molecular orbitals ( $E_{HOMO}$ ) of such systems.

It is necessary to note, that this question was considered by the methods of quantum chemistry in a number of works [10-12]. So, in [10] by the method AM1 the reactive ability indexes of peripheral carbon atoms in  $C_{54}$  (54 carbon atoms, 19 condensed aromatic rings) graphite similar cluster were determined. It's found, that the replacement of the most reactively-capable carbon atom on boron atom results in reduce the reactionary ability of such centres in 3.5 times (from 1.4912<sub>C</sub> up to 0.4144<sub>B</sub>). However the reactionary ability of carbon atoms located on a line increases 1.2÷1.5 times. The authors assert that exactly by such mechanism it's explained the observable on experience inhibition of the processes of boron containing carbons oxidation. From our point of view this seems to contrary to the following arguments. As the oxidation is electrophilic reaction, the oxidizing ability of carbon materials is determined not only by local reduce of reaction ability of the replaced boron atoms in carbon matrix, but also by ionization potential of all system as a whole, i.e. it

depends on energy of some high occupied molecular orbitals located close to Fermi level.

It was [11] established, that the replacement of carbon atoms on boron atoms results in shift of  $E_{\text{HOMO}}$  on 2.6 eV, i.e. causes reduce of ionization potential. Hence, such B - containing clusters should have greater oxidizing ability in comparison with only carbon clusters. We assume the change of E near Fermi level, found in the given work for pure carbon and B-containing clusters, is caused by the carried accounts for graphite-similar clusters, in which the regional carbon atoms were without hydrogen at the edge. It precisely proves to be true by results of accounts of  $E_{\text{HOMO}}$  in clusters  $\text{C}_{24}\text{H}_{12}$  (-8.08eV, 0 at % B),  $\text{C}_{22}\text{B}_2\text{H}_{12}$  (-7.94 eV, 8.33 at. % B) and  $\text{C}_{20}\text{B}_4\text{H}_{12}$  (-7.88 eV, 16.67 at. % B): the introduction of boron atoms (even more 16 at. %) causes the increase of oxidizing ability of such systems, that contradicts experiment. Our results [12] testify, that the  $E_{\text{HOMO}}$  in B-replaced graphite-similar  $\text{C}_{96-n}\text{B}_n\text{H}_{24}$  clusters shifts firstly to more positive energies (ionisation potential decreases) at increase of boron atoms concentration to positive energy area (potential of ionization decreases, i.e. the oxidizing ability increases); at concentration of boron atoms 2÷4 at. %,  $E_{\text{HOMO}}$  energy achieves the maximum (system has the lowest ionization potential, i.e. the largest electron-donor ability); then this energy displaces to negative side, and at boron concentration more than 8÷10% the  $E_{\text{HOMO}}$  becomes more negative, than at only carbon C96 cluster. The similar results are received in [11] also. This indicates carbon materials with concentration of boron atoms more than 8÷10 at. % should have higher thermooxidative stability in comparison with idealized graphite-similar material, that completely prove to be true by experimental data [4,12,13].

It is necessary to note, that for carbon materials with the large contents of several same heteroatom it's not found out the question - which of them (in what position) bears the greatest responsibility for the change of energy characteristics of boundary molecular orbitals ( $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ ) and which are responsible for physical-chemical, electrochemical, catalytic and adsorptive properties of carbon materials at their interaction with other molecular systems or metal ions.

It's not found out also the question on influence of the presence of oxygen atoms introduced in carbon matrix or in functional oxygen-containing peripheral groups on energy characteristics of carbons, containing boron heteroatom. It is known, that for chemical activation of carbon materials the various reagents are applied (for example,  $\text{H}_3\text{PO}_4$ ,  $\text{HNO}_3$  etc.). Pyrolysis and activation in such conditions assumes the introduction of heteroatom (O, N, P) in the large or smaller quantities in carbon material. It is natural to expect, that in real conditions B - containing carbons can also have in a superficial layer some quantity of oxygen in the form of functional groups  $\text{C}=\text{O}$ ,  $>\text{O}$ ,  $\text{OH}$ ,  $\text{COOH}$  and others. It is valid, as follows from the analysis of spectra CXA of B-containing carbons [15] there are strips adequate the signals from as B1s, as O1s, introduced in a molecular skeleton of carbon matrix and the strips are irrespective of the reception method (the use of various precursors –  $\text{B}_4\text{C}$ ,  $\text{BCl}_3$ ,  $\text{B}_2\text{O}_3$ ). It is necessary to note, that the concentration of oxygen atoms in such materials is proportional to concentration of boron atoms. It is necessary also to take into account that the fact, that at concentration of boron atoms in carbon matrix more than 6 at.%, there are appeared in carbon matrix not only the bonds C-B-C and C-B-O, but also the bonds C-B-B, and the amount of the latter ones was shown with the CXA and NMR  $^{11}\text{B}$  to be proportional to boron atoms quantity in carbon [4].

## Results and Discussion

With the purpose of more detailed research of possible influence of concentration and position of boron atoms in a molecular matrix of B-containing carbon materials on their thermooxidative stability we have made the calculation by the AM1 method and in the present report there are given the results of electronic structure as for graphite-similar  $C_{96-n}B_n$  cluster (7.2 at.% B), where boron atoms are in various positions of molecular skeleton, as for  $C_{96-n}B_n$  ( $n \rightarrow 2-8$  at. % B) clusters with  $n$  similar boron atoms.

For  $C_{96-n}B_n$  cluster (Fig.1a) there were calculated energy spectrum (Fig. 1b), local density functions of carbon atoms (C) and boron (B) (fig.1c) atoms, and also the local density functions for various boron atoms positions in a molecular skeleton (fig.1d). As it is visible from a fig.1 the energy of boundary molecular orbitals level ( $E_{i,HOMO}$  and  $E_{i,LUMO}$ ) for boron and carbon atoms are identical and are in the region of -6.8 eV and -3.7eV, accordingly. Taking into account, that in  $C_{96-n}B_n$  cluster the boundary molecular orbitals are conjugated  $\pi$ -orbitals, the obtained data testifies undoubtedly to the unified conjugated system as for carbon, as boron atoms. However, the intensity of local density function of carbon atoms surpasses considerably those for boron atoms, that indicates authentically that in such cluster the donor-acceptor properties are defined, in main, by properties of  $\pi$ -conjugated carbon cluster system.

With given on a fig.1d spectra of local density function of boron atoms, taking place in various positions in cluster  $C_{96-n}B_n$ , it is visible, that the greatest contribution in electron-donor properties cluster is brought in boron atoms in position  $B_{2a}$  and  $B_3$ , a little bit smaller - boron atoms  $B_P$  and  $B_1$  and  $B_4$ , whereas the contribution of boron atoms  $B_H$  and  $B_2$  is not essential. It is necessary, however, to emphasize, that if in a carbon matrix there are some boron atoms identical on a state, then, due the uniform conjugated system, the local (on boron) density functions in clusters with other arrangement of boron atoms in a molecular cluster skeleton differ, presumably, from the local density functions given on a fig. 1d.

It is precisely visible on fig.2a, on which the dependences of the influence of concentration of identical on a nature boron atoms ( $B_H$ -"pyrolytic-similar",  $B_P$  - "pyridine-similar" and in  $B_1$ ,  $B_2$ ,  $B_3$  and  $B_4$ ) on the high occupied molecular orbitals energy  $E_{HOMO}$  in clusters  $C_{96-n}B_n$  are submitted. The structure of some of them is submitted in a fig.3. As it is visible from a fig.2a, with the increase of "pyridine-similar" boron atoms in a carbon matrix the monotonous shift of  $E_{HOMO}$  energy to more positive energies is observed. For all other boron atoms the corresponding dependences have a maximum at boron atoms content 2-4 at.% in a carbon matrix. The further increase of concentration of boron atoms results as it is visible also from the figure, to shift energy  $E_{HOMO}$  to more negative energies, that should promote amplification of thermooxidative stability of such materials.

The received results give the basis to believe, that the steadiest to oxidation boron-containing carbon materials are obtained at replacement of carbon atoms in a carbon matrix on boron atoms in  $B_1$  and  $B_3$  positions and at concentration more than 6 at. %.

Besides taking into account, that real pyrolytical carbon materials which are not exposed to additional oxidation, always contain approximately 4-6 % chemically connected oxygen in the form of groupings  $C=O$  and  $>O$  or functional groups OH, COOH and CHO, there were carried out the computations of energy characteristics of graphite-similar clusters, containing as boron as carbon atoms in a molecular skeleton, and also oxygen atoms of a various nature ( $C_{96-n-m}B_nO_m$ ): in carbonyl ( $C=O$ ),

phuranic ( $>O$ ), hydroxyl (OH) and carboxyl (COOH) groups. The structure of some such clusters is submitted also in a fig. 3.

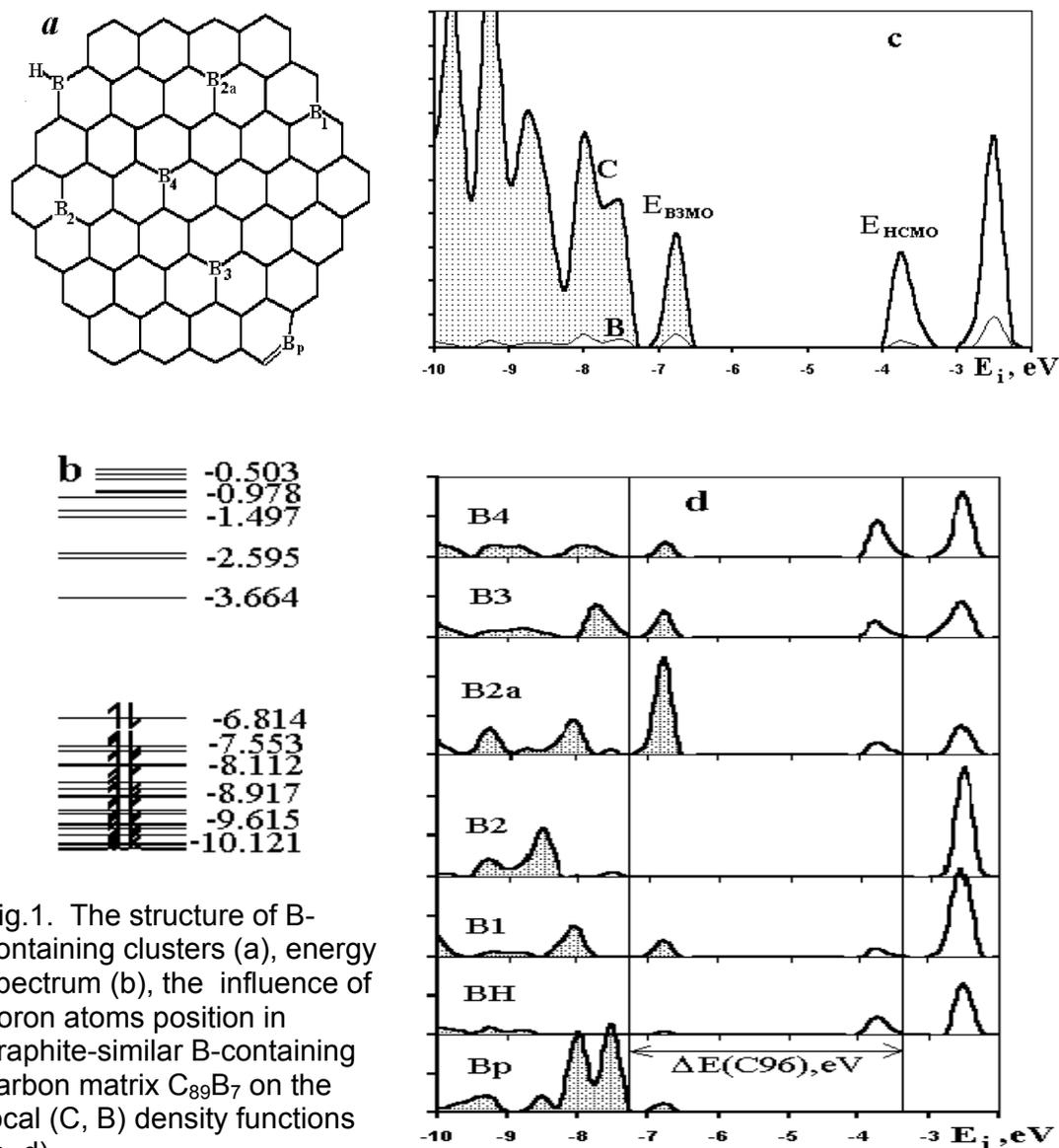


Fig.1. The structure of B-containing clusters (a), energy spectrum (b), the influence of boron atoms position in graphite-similar B-containing carbon matrix  $C_{89}B_7$  on the local (C, B) density functions (b, d).

The question on the influence of O-containing groups on energy characteristics of carbon clusters is most in detail considered in [16]. It was established in it, that the introduction of functional groups OH, COOH or CHO in carbon matrix results in insignificant and monotonous change of boundary molecular orbitals energies  $E_{HOMO}$  responsible for electron-donor cluster properties. As it was expected, the introduction of electron-donor groups (OH) into carbon matrix moves monotonously the low occupied molecular orbitals energy  $E_{HOMO}$  to more positive energies, while the introduction of electron-acceptor groups (COOH, CHO) – to more negative energies, i.e. causes the increase or the inhibition, accordingly, of oxidizing properties of carbon materials.

At introduction of carbonyl (C=O) or phuranic-similar ( $>O$ ) oxygen atoms into O-containing molecular skeleton of cluster the dependence of  $E_{HOMO}$  on the amount of O-containing groups, as well as the similar dependence for B-containing

clusters, passes through a maximum at 3-6 at. % concentration of oxygen. Most likely, it is associated with the including of 2p-electrons of oxygen of phuranic and carboxyl type (as opposed to other oxygen types) into common  $\pi$ -conjugated system of cluster's condensed rings.

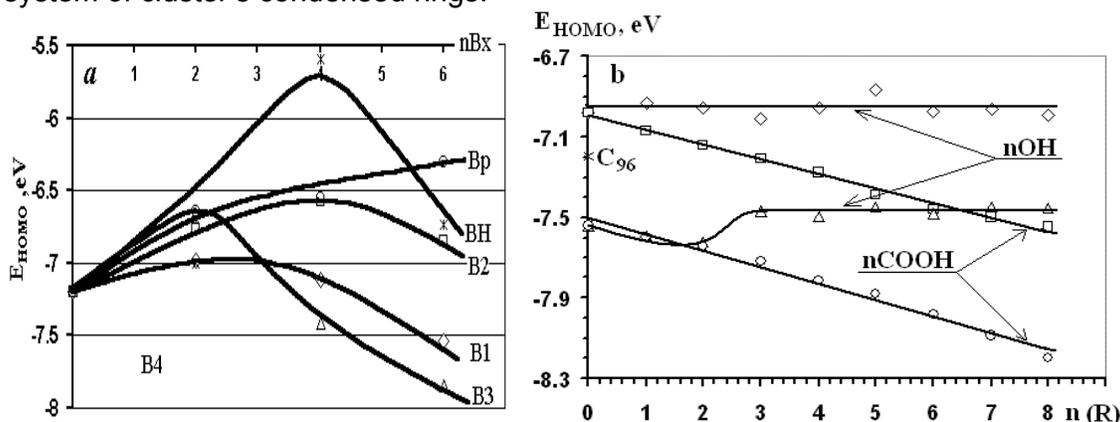


Fig.2. The influence of a) the concentration of similar boron atoms and b) the quantity of groups R (COOH and OH) on the  $E_{HOMO}$  energy of  $C_{96-n}B_nR_m$  clusters.

Corresponding energies  $E_{HOMO}$  of the data of mixed B, O-clusters, containing oxygen in carbonyl (C=O) or "phuranic-similar" (>O) groups are given in the table. As it is visible from the table, in many cases these electron-donor molecular orbital energies ( $E_{HOMO}$ ) are displaced to more negative energies in comparison with  $E_{HOMO}$  only carbon cluster  $C_{96}$  (or clusters containing only boron or oxygen heteroatom). The difference in energies  $E_{HOMO}$  for initial B- or O-containing carbons and the carbons containing a various ratio of B and O can achieve about 1eV, that explains, from our point of view, synergism of inhibition simultaneous action of B and O heteroatom on the processes of thermooxidation of B-,O-containing carbon materials.

The table.

The energy  $E_{HOMO}$  of  $C_{96-n-m}B_nO_m$  and  $C_{99-n-m}B_nCO_m$  clusters

B/O		0	1	2	3	4	5	6
0	>O	-7.20	-6.80	-6.53	-5.96	-5.67	-7.07	-7.29
	C=O		-6.94	-7.00	-6.32	-5.76	-7.68	-7.78
1	>O	-7.10	-6.35		-6.06		-7.05	
	C=O		-6.65		-6.31		<b>-7.68</b>	
2	>O	-6.98		-6.40		-6.74		-6.86
	C=O			-6.44		<b>-7.47</b>		-6.73
3	>O	-6.97	-7.00		-7.02		-6.67	
	C=O		<b>-7.20</b>		<b>-7.47</b>		<b>-7.46</b>	
4	>O	-7.20		-6.81		-6.65		-6.06
	C=O			-7.11		<b>-7.28</b>		-7.19
5	>O	-7.35	-6.89		-6.35		-6.67	
	C=O		-6.88		<b>-7.46</b>		<b>-7.43</b>	
6	>O	-7.63		-6.48		-6.76		-6.51
	C=O			-6.69		-7.43		-7.08

The influence of hydroxyl (OH) and carboxyl (COOH) functional groups introduction into B-containing clusters is visible from a fig.2b. The energies  $E_{\text{HOMO}}$  of  $\text{C}_{94}\text{B}_2(\text{OH})_n$  and  $\text{C}_{88}\text{B}_6(\text{OH})_n$  clusters practically not change from those ones of clusters  $\text{C}_{94}\text{B}_2$  and  $\text{C}_{88}\text{B}_6$  while for  $\text{C}_{94}\text{B}_2(\text{COOH})_n$  and  $\text{C}_{88}\text{B}_6(\text{COOH})_n$  clusters the monotonous shift of  $E_{\text{HOMO}}$  to more negative energies is observed. Comparing the received energies  $E_{\text{HOMO}}$  for  $\text{C}_{94}\text{B}_2\text{R}_n$  and  $\text{C}_{96}\text{B}_6\text{R}_n$  ( $\text{R} \rightarrow \text{OH}, \text{COOH}$ ) is possible to make a conclusion, that electron-donor properties of hydroxyl group influence insignificantly on the boundary molecular orbitals energies of clusters. The introduction of electron-acceptor carboxyl functional groups into B-containing clusters results in the even greater procrastination of electronic density from a molecular skeleton of cluster, as causes observed change of  $E_{\text{HOMO}}$ .

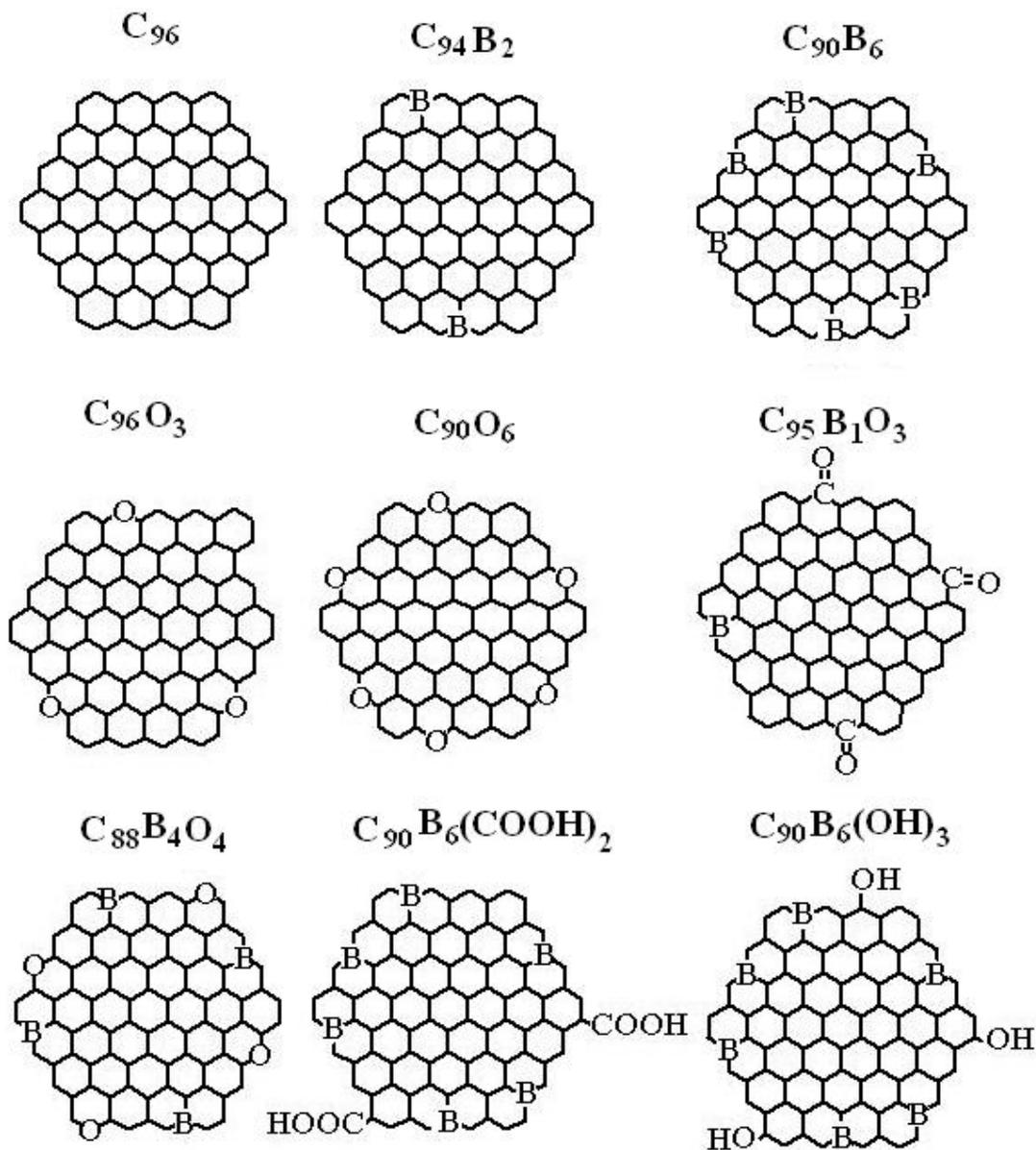


Fig.3. Structure of model clusters.

Hence, the received results give the basis to believe, that oxidized carbons (at a sufficient degree of oxidation) can be used as stable to thermooxidation carbon materials interchangeably with B-containing carbons.

### Conclusions

Thus, the submitted data allow from the uniform point of view on the basis of the analysis of a molecular structure, to explain the reasons of strengthening common influence of electron-donor properties of B, and also B-,O-containing carbon clusters on the processes of inhibition of thermooxidation of carbon materials. The received results testify also, that for reception of carbon materials with raised thermo oxidative stability it is necessary to supervise the processes of synthesis so that to reach optimal boron and oxygen ratio.

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