Theoretical study of the influence of heteroatoms (N, B, Si) on the interaction of aluminum and iron clusters with a carbon graphene-like plane

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Abstract

Metal composites modified with various heteroatoms, such as N, B, Si, are used to obtain matrix composites with specific parameters with the strongest adhesion-cohesion bonds between metal atoms and carbon nanoparticles. Such functionalized heteroatoms carbon nanoparticles are promising for metal composites.

The aim of the study was to determine the effect of temperature on the chemical interaction of aluminum and iron clusters with native, boron-, silicon- and nitrogen-containing graphene-like planes (GLP).

The values of the energy effect of reactions (ΔE_{react}) of Al_2 and Fe_2 dimers with native and modified GLP, as well as the dependence of their free Gibbs energy on temperature are calculated. The highest positive value of the energy effect of the reaction of the native graphene-like plane was set for the aluminum dimer.

The energy effect of the reactions between GLP $\text{C}_{22}\text{B}_2\text{H}_{12}$ and the dimer Fe_2 and is -210.5 kJ/mol. The energy effect of the reactions between GLP $\text{C}_{22}\text{B}_2\text{H}_{12}$ and dimer Al_2 is much smaller (-2.4 kJ/mol). For the interaction of GLP $\text{C}_{22}\text{N}_2\text{H}_{12}$ with dimers Al_2 and Fe_2 , the energy effect of the reaction in the result of calculations: -100.4 and -94.6 kJ/mol, respectively.

For silicon carbide cluster with dimers Al_2 and Fe_2 , they turned out to be exothermic with energy effects of -25.1 and -136.6 kJ/mol, respectively. In addition, of all the cases considered, for the interaction of GLP $\text{C}_{22}\text{N}_2\text{H}_{12}$ with Al_2 , the curve of the Gibbs free energy of the reaction on temperature is below the curve for the iron dimer.

Introduction

The creation of metal-matrix composite materials modified with carbon nanomaterials is a promising area of modern science. In obtaining such composites, powder metallurgy methods are most often used. This allows to achieve the optimal distribution of nanoparticles in the metal matrix without their destruction. The research on the creation of composites based on Al, Mg, Ti is the most active because these metals have a fairly high physical, mechanical and technological properties. This has been studied by many researchers [1–7].

Carbon nanoparticles can be both a strengthening phase and modifiers of the first kind, changing the crystal structure of the matrix metal. The main problem is the formation of the strongest adhesive bonds between metal atoms and carbon nanoparticles in the metal composite. Their formation is complicated by the fact that in the initial state carbon nanomaterials are chemically inert. Therefore, before using them as a reinforcing phase, it is necessary to make the appropriate modification. One method of such modification may be the addition of a carbon matrix with various heteroatoms, such as N, B, Si. The influence of such heteroatoms on the interaction of the carbon surface with metals was studied in the last century on the examples of the interaction of carbon fibers with metals in the manufacture of fiber-

reinforced metal composites. This effect has been studied [8]. In view of this, it is quite probable that carbon nanoparticles doped with heteroatoms can also form stronger adhesive bonds with metals. Thus, carbon nanoparticles functionalized by heteroatoms are promising for various metal composites.

It is advisable to predict the surface properties of such carbon nanomaterials supplemented by heteroatoms (N, B, Si) upon contact with various metals (Al, Fe) by modeling such interaction by methods of quantum chemistry.

The aim of the work was to determine the effect of temperature on the chemical interaction of aluminum and iron clusters with native, boron-containing, silicon-containing and nitrogen-containing graphene by the methods of quantum chemistry, using the calculation scheme of density functional theory with B3LYP functional and basic set 6-31G (d, p).

Objects And Methods Of Calculation

A polyaromatic molecule coronene with $C_{24}H_{12}$ was selected as the initial graphene-like plane (GLP) (Fig. 1, a). Models of modified GLP were formed by replacing two carbon atoms with nitrogen or boron atoms, forming clusters with the composition, $C_{22}N_2H_{12}$, and $C_{22}B_2H_{12}$ (Fig. 1, b, c). The $C_{12}Si_{12}H_{12}$ cluster was used for the silicon carbide model (Fig. 1, d).

The simulations were performed on the example of the interaction of the coronene molecule and its heteroatomic derivatives with diatomic clusters of aluminum (Fig. 2, a) and iron. The multiplicity of the latter is 9 (Fig. 2, b).

When these dimers interact, their atoms form chemical bonds with carbon atoms and graphene-like heteroatoms. In this case, as calculations show, one of the carbon atoms leaves the plane of the conjugate aromatic system. This demonstrates the initial stage of destruction of this graphene-like plane with the formation of aluminum and iron carbide. Therefore, a number of identical reactions for the addition of dimers of the corresponding metals (Me_2) to graphene-like nanocluster (GLN) were considered. They can be represented schematically as below:

The energy effects of the reaction (ΔE_{react}) were calculated at a temperature of 0 K, and without taking into account the energy of zero oscillations (ZPE), according to scheme (1), by to the following formula (2):

$$\Delta E_{react} = E_{tot}(Me_2GLN) - (E_{tot}(Me_2) + E_{tot}(GLN)), \quad (2)$$

where $E_{tot}(Me_2GLN)$ is the total energy of the product of the interaction of the metal dimer with GLN, $E_{tot}(Me_2)$ is the total energy of the metal dimer, $E_{tot}(GLN)$ is the total energy of the graphene-like nanocluster.

The values of the free Gibbs reaction energy (ΔG_{react}) in the temperature range from 50 to 1800 K were also calculated:

$$\Delta G_{react} = G^T((Me_2GLN)-(G^T(Me_2) + G^T(GLN))), \text{ (3)}$$

where $G^T = E_{tot} + ZPE + G^T_{corr}$ E_{tot} is the total energy of the corresponding optimized structure, ZPE (zero point vibrational energy) is the energy of zero oscillations of the optimized structure, G^T_{corr} is the thermodynamic correction of the free Gibbs energy [10].

Calculations were done using the GAMESS (US) program [10] within the theory of density functional (DFT) with B3LYP functional [11–12] and 6-31G basic set (d, p).

Results And Discussion

At the beginning, the interaction of the initial graphene-like plane with dimers of aluminum and iron is considered.

The Fig. 2, a, shows, that due to the interaction of the aluminum dimer with the coronene molecule, the plane of the latter is significantly deformed. One of the aluminum atoms binds simultaneously to three carbon atoms, and the Al–C bonds are almost identical, and their length ranges from 1.87 to 1.88 Å. Another aluminum atom has only one Al – C bond with a length of 2.02 Å, which is less than the length of the bond between two aluminum atoms in the dimer, (2.57 Å) (Fig. 2, a).

The energy effect of reaction (1), calculated by formula (2), has a positive value and equals to 289.2 kJ/mol (see Table 1). This indicates a small thermodynamic probability of this reaction in the direction of formation of the reaction product at 0 K.

Table 1
Energy effects (ΔE_{react}) of the reaction of interaction of metal dimers with graphene-like planes (kJ/mol)

Gross composition of graphene-like planes	Dimers of metals	
	Al ₂	Fe ₂
C ₂₄ H ₁₂	+289.2	+204.3
C ₂₂ N ₂ H ₁₂	100.4	94.6
C ₂₂ B ₂ H ₁₂	2.4	210.5
C ₁₂ Si ₁₂ H ₁₂	25.1	136.6

According to the results of the calculation of the free Gibbs energy of the reaction calculated by formula (3), at 50 K this value as well as the energy effect is positive and equals to 283.0 kJ/mol, with increasing

temperature up to 1800 K the value of ΔG_{react} increases to 500.4 kJ/mol, i.e the degree of endothermicity of reaction (2) increases (Fig. 4, a).

When the nanocluster of iron (Fe_2) interacts with the coronene molecule, the structure of the formed product does not differ significantly from the structure of the previous one with the aluminum cluster (Fig. 3). In particular, one of the iron atoms forms three covalent bonds with carbon atoms with a length of 1.81 to 1.89 Å (Fig. 3, b), between the iron atoms, like the aluminum atom, there is a carbon atom. However, another iron atom forms two covalent bonds with the carbon atoms of the coronene molecule, in contrast to the aluminum atom (Fig. 3, a), where the latter is bound to the GLP by only one covalent bond.

The energy effect for the reaction with the iron dimer, calculated as in the previous case according to formula (2), is also positive and is +204.3 kJ/mol, which is 84.9 kJ/mol less than for the reaction involving the Al_2 dimer (see Table 1).

The Fig. 4, a, shows, that the curves of the free Gibbs energy of the reaction of the coronene molecule with aluminum and iron are almost parallel to each other. This means that, as in the previous case, with the temperature increase, the values of ΔG_{react} also increase. In this case, the curve for the reaction with iron is lower than for a similar reaction with aluminum, which indicates that these two reactions are endothermic, but with the participation of iron, the degree of its endothermicity is less.

The next task was to find out how the above reactions with aluminum and iron are affected by the presence of two nitrogen atoms, which are embedded instead of two carbon atoms in a vapor position relative to each other in the central hexagon of the coronene molecule (Fig. 1, b).

The product of the interaction of the aluminum dimer with this GLP is structurally similar to the one discussed above (Fig. 3, a) where one of the aluminum atoms is bound to two carbon atoms by bonds of length 1.88 Å, as well as to the nitrogen atom of the GLP. 1.89 Å. As in the previous case, a carbon atom is placed between the aluminum atoms, and the second aluminum atom is connected to the rest of the molecule by one covalent bond, the length of which is also 1.88 Å (Fig. 5, a). However, the Al – C bond is placed perpendicular to the plane of the coronene derivative, in contrast to the product shown in Fig. 3, a.

The energy effect of the reaction involving an aluminum dimer and a nitrogen-containing derivative of coronene, as can be seen from the Table 1, has a negative value in contrast to a similar reaction involving a molecule of coronene and is 100.4 kJ/mol. Values of ΔG_{react} from 50 to 690 K are negative, and above this temperature are positive and with the temperature increase the value of Gibbs free energy of this reaction increases (Fig. 4, b).

In turn, the reaction product of the nitrogen-containing coronene with the iron dimer (Fig. 5, b) is similar in structure to the product of the interaction of Al_2 with the coronene (Fig. 3, b). It is also characterized by the fact that one of the iron atoms is bonded by covalent bonds with two carbon atoms, lengths from 1.77 to 1.87 Å, as well as with a nitrogen atom by a bond length of 1.87 Å. Another iron atom is

connected to carbon atoms by two bonds, 1.89 and 1.99 Å in length. The value of ΔE_{react} for the reaction of nitrogen-containing GLP with iron dimer, as well as for the reaction with aluminum dimer, has a negative value, but it is 5.8 kJ/mol less (see Table 1) and is 94.6 kJ/mol. Analysis of the Gibbs free energy curve of this reaction on temperature shows that, as for the previous reaction with aluminum (Fig. 4, b), the value of ΔG_{react} increases with increasing temperature. The peculiarity of the reaction with iron is that at low temperature (50 K) the Gibbs energy is 2.4 kJ/mol lower (92.9 kJ/mol) than the same value for the reaction with aluminum (90.5 kJ/mol). Above 170 K, the temperature dependence curve ΔG_{react} with iron becomes higher than for the reaction with aluminum (Fig. 3, b). In the case of the coronene, the opposite relationship was observed – the free Gibbs reaction energy was higher for aluminum (Fig. 3, a).

It was further investigated how the above reactions with aluminum and iron are affected by the presence of two boron atoms (Fig. 1, c), which were placed instead of two nitrogen atoms in a vapor position relative to each other in the central hexagon of the corona derivative.

As can be seen from Fig. 6, a, the product of the interaction of the aluminum dimer with boron-containing derivative of coronene, differs significantly from the previous nitrogen-containing (Fig. 5, a). In particular, aluminum atoms do not form covalent bonds with boron atoms, but only with carbon atoms longer than 2 Å. In this case, the central hexagon of the structure shown in Fig. 1, c, due to the interaction turns into a pentagon. However, as in previous cases, there is a carbon atom between the aluminum atoms.

The energy effect of the reaction of product formation, which is shown in Fig. 6, a, has a slight negative value equal to 2.4 kJ/mol, at 0 K (see Table 1), which is 98.0 kJ/mol less than the same value for the nitrogen-containing product with aluminum.

The free Gibbs energy of this reaction at 50 K is +1.9 kJ/mol and with a further increase in temperature, as shown in the graph shown in Fig. 7, ΔG_{react} continues to grow.

The next product of the interaction of boron-containing derivative of coronene and iron dimer (Fig. 6, b) also differs significantly from similar products of interaction of iron dimers with molecules of coronene and its nitrogen-containing derivative (Fig. 3, b, and Fig. 5, b). In particular, iron atoms form covalent bonds with carbon atoms with a length of 1.98 Å, and also coordinate with the atoms of boron-carbon hexagons of the graphene-like plane with an interatomic distance from 2.17 to 2.46 Å. It should be noted that, as in the previous case, when interacting with an aluminum dimer, the central hexagon of the boron-containing derivative of the coronene is transformed into a pentagon (Fig. 6, b).

The magnitude of the energy effect of this reaction is also negative as in the case of aluminum, but it is an absolute value of 208.1 kJ/mol higher and is 210.5 kJ/mol (see Table 1). As we can see in Fig. 7, a, the Gibbs free energy dependence curve for the boron-containing coronene reaction and the iron dimer is almost parallel to a similar curve for the aluminum dimer. In this case, at temperatures below 1300 K, the value of ΔG_{react} is negative, at 50 K its value is 206.8 kJ/mol, and at 1800 K it is positive and its value equals to +70 kJ/mol.

The thermodynamic parameters of the reaction of silicon-containing coronene with dimers of aluminum and iron were also investigated. The molecule of silicon-containing coronene, in contrast to previous hetero derivatives differs. The difference is that there are twelve carbon atoms, instead of two, are replaced by silicon atoms. That is, there is an alternation of carbon and silicon atoms and their equal number in the molecule allows us to consider it as a model of silicon carbide.

The product of the interaction of a silicon derivative with an aluminum dimer is characterized by the fact that one of the aluminum atoms interacts with two silicon atoms with bond lengths of 2.4 Å (Fig. 8, a). Between the aluminum atoms, as in all previous cases, there is a carbon atom with Al–C bond lengths of 1.85 and 1.94 Å. In addition, the second aluminum atom coordinates with the silicon atom at a distance of 2.7 Å.

The energy effect of this reaction has a negative value and is 25.1 kJ/mol, and the free Gibbs energy of the reaction up to 190 K also has a negative value and at 50 K it has a value of 20.6 kJ/mol. However, above this temperature, ΔG_{react} becomes positive and at 1800 K it becomes +216.0 kJ/mol.

Similar to the previous one, the reaction product formed by interaction with an iron dimer (Fig. 8, b), in particular, like the iron atom discussed above, forms two chemical bonds with a length of 2.26 Å and silicon atoms. Its peculiarity is that the second iron atom forms a covalent bond with a carbon atom with a length of 2.06 Å.

The energy effect of this reaction, as in the case of aluminum, has a negative value, which in absolute value is 111.5 higher than the same value for the aluminum dimer and is 136.6 kJ/mol (see Table 1). The Fig. 7, b, shows, that the curve ΔG_{react} for the reaction with Fe_2 is parallel to a similar curve for the reaction with the aluminum dimer. Up to 980 K the free Gibbs energy is negative and at 50 K it is 133.7 kJ/mol, and at 980 K it is positive, and at 1800 K it is + 105.3 kJ/mol.

The Table 1 shows that the highest value of ΔE_{react} chemical interaction is for the native graphene-like plane +289.2 kJ/mol both in the case of aluminum dimer, +204.3 kJ/mol, and in the interaction with iron dimer for nitrogen-containing coronene this value is the lowest of all considered for the aluminum dimer, and is 100.4 kJ/mol, and for the iron dimer, it is slightly smaller and is 94.6 kJ/mol.

For the boron-containing plane, this value has a negative value of 2.4 kJ/mol, and in the case of an iron dimer, this value is the lowest of all considered and is 210.5 kJ/mol. For silicon-containing - 25.1 kJ/mol (for Al_2) and - +136.6 kJ/mol (for Fe_2).

Conclusions

The results of the calculations show that the highest value of ΔE_{react} chemical interaction is +289.2 kJ/mol for the native graphene-like plane in the case of aluminum dimer, +204.3 kJ/mol, for silicon-containing is 25.1 kJ/mol, for boron-containing plane this value is negative 2.4 kJ/mol, and for nitrogen-containing it is the lowest and is 100.4 kJ/mol. And the lowest value of the energy effect of the reaction

of all the considered cases is characteristic of the interaction of boron-containing coronene with the iron dimer of 210.5 kJ/mol.

Therefore, the presence of nitrogen atoms in the nanocarbon matrix best promotes interaction with the aluminum nanocluster, and the presence of boron atoms in the nanocarbon matrix determines the largest in absolute value E_{react} of the interaction with the iron nanocluster. In addition, of all the cases considered, only for the nitrogen-containing coronene is it observed that the curve of the Gibbs reaction energy on the temperature for aluminum is lower than the similar curve for the iron dimer.

Declarations

Conflict of Interests

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Competing Interests

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Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Terets M.I., Ushakova L.M., Zhuravskiy S.V., Sementsov Yu.I., Lobanov V.V., Filonenko O.V., Kuts V. S. and Kartel M.T. The first draft of the manuscript was written by Demianenko E.M. and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Tables

Table 1 Energy effects (ΔE_{react}) of the reaction of interaction of metal dimers with graphene-like planes (kJ/mol)

Gross composition of graphene-like planes	Dimers of metals	
	Al ₂	Fe ₂
C ₂₄ H ₁₂	+289.2	+204.3
C ₂₂ N ₂ H ₁₂	-100.4	-94.6
C ₂₂ B ₂ H ₁₂	-2.4	-210.5
C ₁₂ Si ₁₂ H ₁₂	-25.1	-136.6

Figures

Figure 1

Equilibrium geometry of the coronene (*a*) and its derivatives: nitrogen-containing (*b*), boron-containing (*c*), silicon-containing (*d*).

Figure 2

Equilibrium structure of dimers of aluminum (*a*) and iron (*b*) (here in after interatomic distances in Å).

Figure 3

Equilibrium spatial structure of the products of interaction of the coronene molecule with dimers: aluminum (a) and iron (b)

a

b

Figure 4

Dependence on the Gibbs energy temperature of the reaction of interaction of aluminum and iron dimers with the coronene molecule (a) and its nitrogen-containing derivatives (b).

a

b

Figure 5

Equilibrium spatial structure of the products of interaction of the molecule of nitrogen-containing derivative of coronene with dimers: aluminum (a) and iron (b)

Figure 6

Equilibrium spatial structure of the products of interaction of the molecule of boron-containing derivative of coronene with dimers: aluminum (a), iron (b)

Figure 7

Dependence on the Gibbs energy temperature of the reaction of interaction of aluminum and iron dimers with boron-containing derivative of coronene (a) and its silicon-containing derivative (b)

Figure 8

Equilibrium spatial structure of products of interaction of a molecule of silicon-containing derivative of coronene with dimers: aluminum (*a*) and iron (*b*)