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Anticorrosive Coatings Based on Few-Layer Graphene

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Abstract: In this paper the anticorrosive properties of the few-layer graphene nanostructures were investigated. On the surface of copper and nickel plates the few-layer graphene nanostructures were formed using the CVD (chemical vapor deposition) method. After that, these plates were exposed to the temperature in the air atmosphere. The results of elemental analysis, performed by the EDS (energy dispersive spectroscopy) method showed that the few-layer graphene coated metal plates proved to be more resistant to oxidation than bare metal plates. In addition, we presented computer models and theoretical calculations of the studied systems, performed by the DFT (density functional theory) and MD (molecular dynamics) methods. These results combined with experimental data show the high effectiveness of the protective action of the few-layer graphene against metal corrosion.

Key words: Graphene, anticorrosive coating, CVD method, computer simulation.

1. Introduction

Currently, graphene is known as a two-dimensional material consisting of carbon atoms tightly packed into a honeycomb lattice and having many potential applications due to its unique electrical, thermal, mechanical and barrier properties [1-4].

One of the most important and actual problems is the protection of materials and products from the effects of aggressive environmental factors, gases, and liquids. To solve this problem, the Nobel Prize laureate K. S. Novoselov suggested using graphene as a very effective anticorrosive coating due to its chemical inertness and impermeability [5]. Excellent anticorrosive properties of graphene served as the basis for conducting a series of experiments by various science groups from around the world [6-10]. A popular and optimal method for growing graphene coatings is the CVD (chemical vapor deposition) method. Especially graphene, grown directly on the surface of Cu and Ni by CVD, has a higher resistance to corrosion, in contrast to the transferred graphene [11].

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An anticorrosive graphene coating is able to become very popular for various applications, i.e. it is the effective ultra-thin barrier directly between the metal and the environment.

2. Experimental Section

2.1 Anticorrosive Coatings on the Copper Surface

Before carrying out the basic work, the copper plates were cleaned in a hydrogen medium. Then, the few-layer graphene nanostructures were formed on the copper surface using the CVD method at t = 1,000 °C for 20 min, where benzene was used as a precursor. Fig. 1 shows a typical Raman spectrum confirming presence of the few-layer graphene on the copper surface.

After that out an elemental analysis of samples of bare copper (bare Cu) and few-layer graphene coated copper (G-Cu) was carried by EDS (energy dispersive spectroscopy). The next stage was the oxidation of bare Cu and G-Cu at t = 300 °C for 30 min in the air atmosphere. Oxidized bare Cu and G-Cu samples were analyzed by EDS. Table 1 presents the EDS results of the bare Cu and G-Cu before and after oxidation.

Elemental analysis of the obtained samples showed

that the thin graphene film was able to reliably protect the copper plate from oxidation. The oxygen content after oxidation in bare Cu sample increased to 10.27 at. %, while the amount of oxygen in the G-Cu sample remained unchanged. The carbon content in all copper samples after oxidation remained practically unchanged, which allows us to judge that the few-layer graphene coating is resistant to 300 °C temperature for 30 min in the air atmosphere.

We can also confirm the effectiveness of the protection degree of graphene coating from oxidation, optically assessing differences in color. In Fig. 2 we see optical micrographs of bare Cu and G-Cu after oxidation. Bare Cu, in contrast to G-Cu, acquired the characteristic red-brown color of Cu_2O.

2.2 Anticorrosive Coatings on the Nickel Surface

The nickel plates were previously cleaned by annealing in a vacuum medium. After that, the few-layer graphene nanostructures were grown on the nickel surface by the CVD method at t = 1,000 °C for 20 min. Below is a typical Raman spectrum, confirming the presence of few-layer graphene on the nickel surface (Fig. 3).

The next stage was the oxidation of bare nickel (bare Ni) and the few-layer graphene coated nickel (G-Ni) at t = 300 °C, 400 °C, 500 °C for 10 min in the air atmosphere. The obtained samples were analyzed by the EDS method. According to the quantitative composition of the oxygen shown in Fig. 4a, we

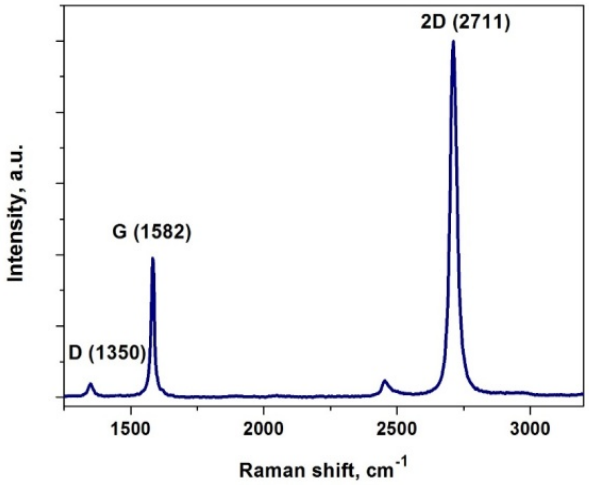
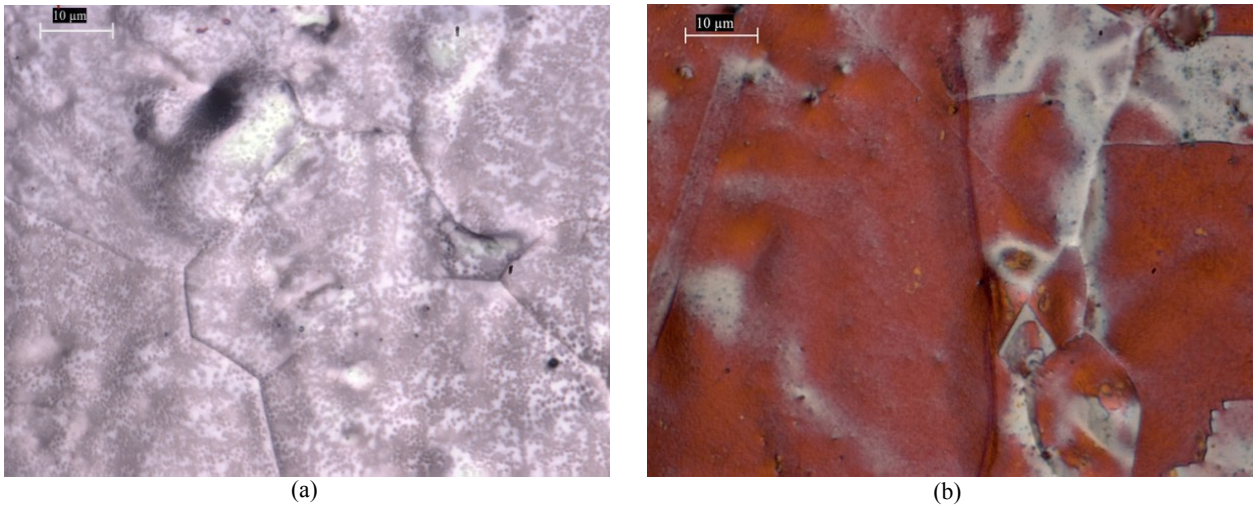


Fig. 1 Typical Raman spectrum of the few-layer graphene on the copper surface.

Table 1 The EDS results of the bare Cu and G-Cu before and after oxidation.

Elements	Bare Cu		G-Cu	
	Before oxidation	After oxidation	Before oxidation	After oxidation
Cu (at. %)	99.93	89.71	67.9	69.7
C (at. %)	0.03	0.02	32.09	30.27
O (at. %)	0.04	10.27	0.01	0.03



(a) (b)

Fig. 2 Optical micrographs after oxidation of (a) G-Cu and (b) bare Cu.

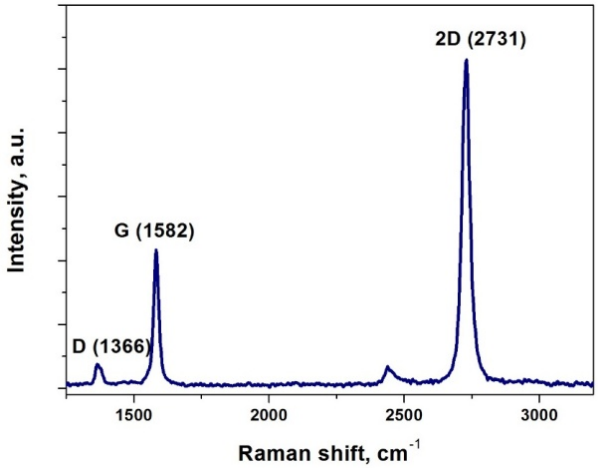


Fig. 3 Typical Raman spectrum of the few-layer graphene on the nickel surface.

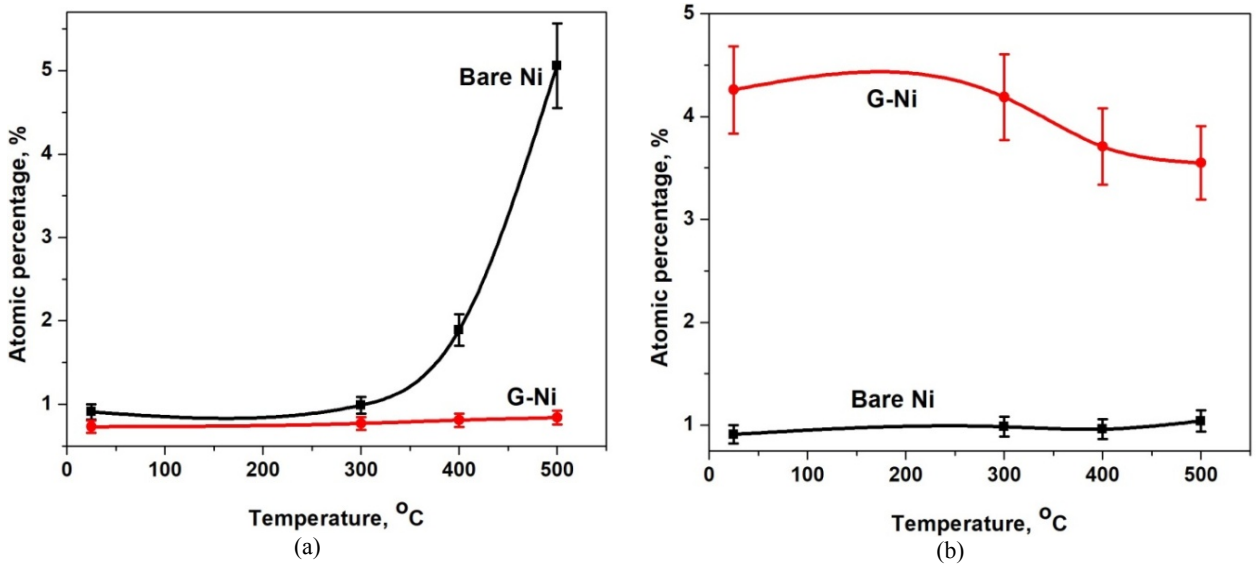


Fig. 4 (a) Quantitative composition of oxygen; and (b) quantitative composition of carbon.

determined that G-Ni oxidizes at 1.2 times slower than bare Ni, 1.3 times at 300 °C, 2.3 times at 400 °C, and 6.0 times at 500 °C. According to the quantitative composition of the carbon shown in Fig. 4b, we concluded that a small amount of carbon from the G-Ni surface is burned with increasing temperature to 500 °C. Nevertheless, burning carbon from the G-Ni surface in this temperature range does not affect the anticorrosive properties of the coatings.

According to the optical micrographs presented in Fig. 5, it can be seen that the greatest effect is observed at t = 500 °C, where bare Ni, in contrast to G-Ni, has a blue-black color confirming more intensive oxidation of nickel. We can see an increase in oxidized sites in G-Ni as the temperature increases.

3. Computer Simulation

To confirm theoretically the effectiveness of the graphene's protective action against metal corrosion, we used two basic possibilities for the penetration of an oxygen into the copper surface area closing by the graphene (directly through graphene and through the gap between the substrate and graphene).

Bunch et al. [12] have reported that monolayer graphene is practically impermeable to standard gases, including the helium. However, this option was simulated. We used computer simulation methods of the investigated nanostructures based on DFT (density

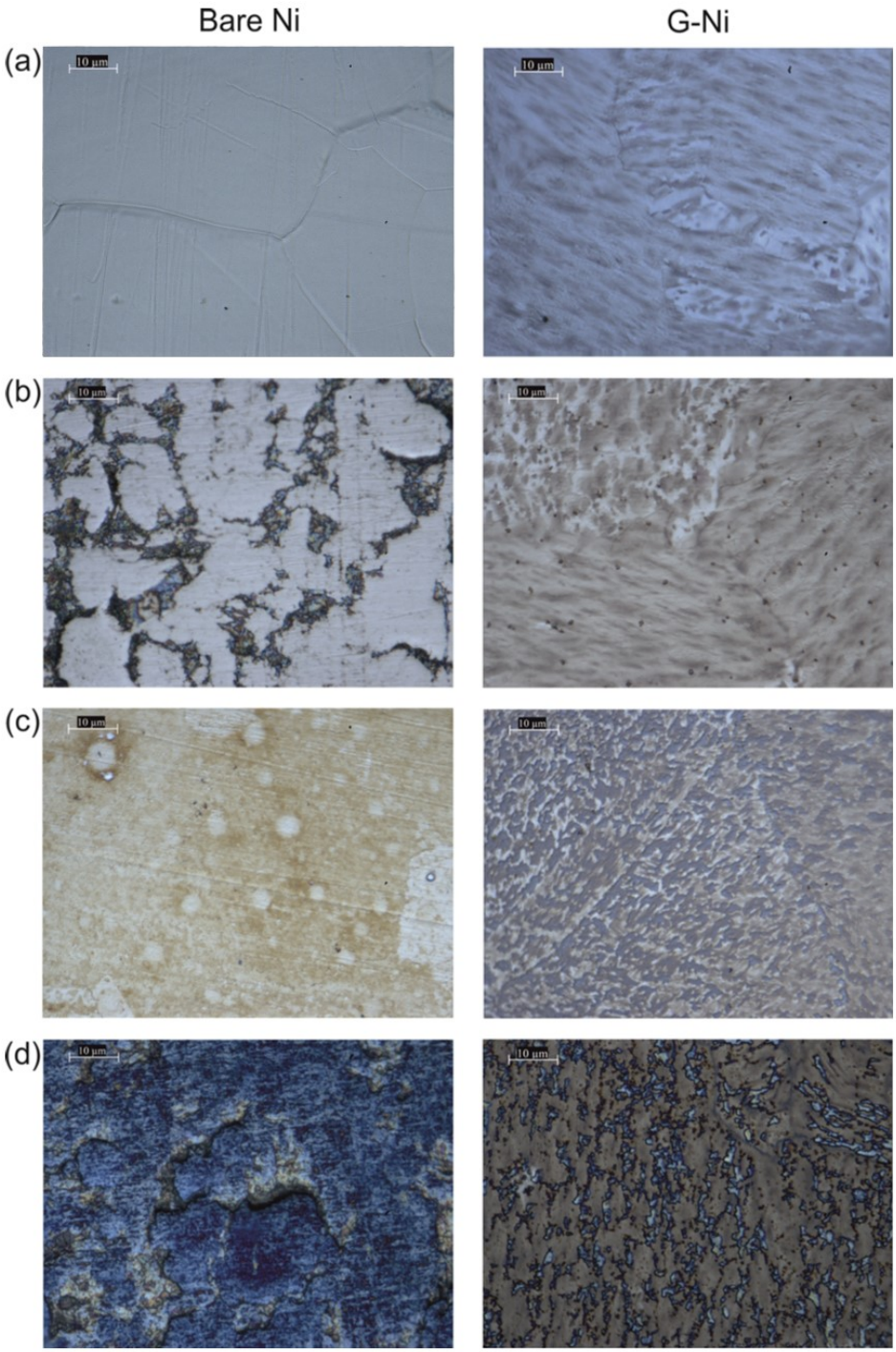


Fig. 5 Optical micrographs of bare Ni and G-Ni after oxidation at: (a) t = 25 °C, (b) t = 300 °C, (c) t = 400 °C and (d) t = 500 °C.

functional theory) and MD (molecular dynamics). The DFT method proved to be an effective tool in previously published works to describe the energy and structural characteristics of graphene nanostructures, including functionalized ones [13-15]. Calculations showed that for the penetration of the oxygen molecule directly through the graphene, the energy barrier is very high even with the most favorable orientation of the molecule—when the axis is perpendicular to the graphene plane and passes

through the center of the hexagon (Fig. 6). For the others orientations, the barrier is even higher.

For penetration opportunity of oxygen through the gap between the substrate and the graphene are considered two basic orientations of oxygen molecules when entering the gap: the axis of the molecule is parallel to the graphene's edge and the axis of the molecule is perpendicular to the graphene's edge.

Computer simulation and calculations showed the presence of the potential barrier for the entry of the molecule in the area gap of grapheme-substrate (Fig. 7). It is shown that the barrier height for the O_2 molecule to enter the space between the substrate and the graphene is strongly dependent on the molecule orientation. It is about twice as less as for the orientation in which the axis of the molecule is perpendicular to the graphene's edge. Nevertheless, even in this case, the probability of oxygen penetration into the graphene-enclosed zone is negligible.

The calculations' results of the dependence of the energy barrier (ΔE) on the distance (Z) through the gap between the substrate and graphene for two main orientation types, when the axis of the O_2 molecule is parallel to the graphene's edge and when the axis of the O_2 molecule is perpendicular to the graphene's edge are presented in Table 2.

For the nickel, the results of computer simulation and calculations will be similar and also indicate the presence of a high potential barrier, which is not capable of passing oxygen molecules.

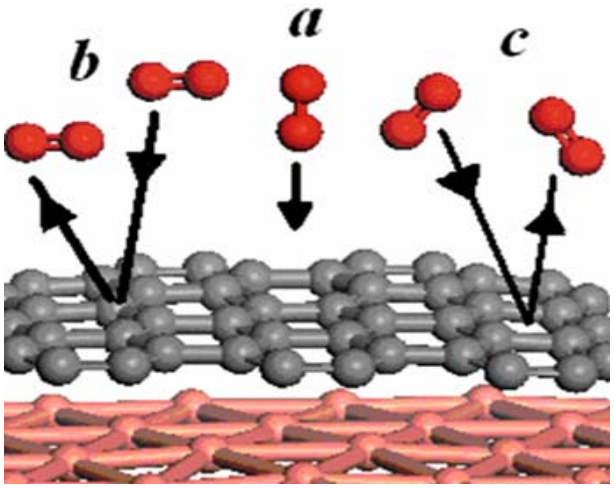


Fig. 6 Computer simulation of the O_2 molecule passage directly through graphene. Energy barriers for different orientations of the molecule: E = (a) 34.3 eV, (b) 40 eV, (c) 38 eV.

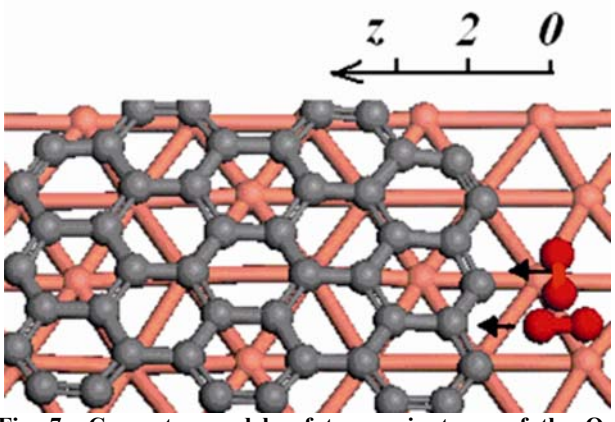


Fig. 7 Computer models of two main types of the O_2 molecule orientation.

Table 2 Dependence of ΔE on Z through the gap between the substrate and graphene for two possible orientations of the O_2 molecule.

Z, Å	ΔE, eV	
	The axis of the O_2 molecule is parallel to the graphene's edge	The axis of the O_2 molecule is perpendicular to the graphene's edge
0	0	0
0.5	1.5	-
1.0	4.1	4.2
2.0	14.6	6.9
3.0	11.6	5.6
3.5	11.4	5.5

4. Conclusions

In this paper an experimental and theoretical study of few-layer graphene coating protecting against corrosion of metals was carried out. In the course of the work, the few-layer graphene nanostructures were obtained in the CVD installation. Experiments were carried out on the oxidation of copper and nickel plates under the influence of temperature in the air atmosphere. The copper plates were oxidized at t = 300 °C for 30 min, the nickel plates were oxidized at t = 300 °C, 400 °C, 500 °C for 10 min. The obtained samples were investigated by a scanning electron microscope (EDS method), an optical microscope, and Raman spectroscopy. Elemental analysis of copper plates showed that the oxygen content after oxidation in bare Cu sample increased to 10.27 at. %, while the amount of oxygen in the G-Cu sample remained unchanged. Elemental analysis of nickel plates showed that G-Ni at t = 25 °C is oxidized in the air atmosphere 1.2 times slower than bare Ni, 1.3 times at 300 °C, 2.3 times at 400 °C, 6.0 times at 500 °C.

Computer models of the studied systems were created and calculations of the barrier properties of graphene against the penetration of oxygen by the DFT and MD method were performed. Computer simulation and calculations showed the presence of a high potential barrier for the entry of the oxygen molecule directly through graphene and through the gap between the substrate and graphene.

Acknowledgments

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