ANNOTATION
of thesis for the degree of Doctor of Philosophy (PhD) in the specialty 6D071000 - "Materials Science and Technology of New Materials"

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Anticorrosion protective coatings based on graphene nanostructures

General characteristics of the study

From general point of view, the properties of anticorrosion protective coatings based on graphene nanostructures have been studied in this work.

The first section is devoted to the literature review, which includes the topics on the corrosion of materials and methods of corrosion protection, the structure and basic properties of graphene, methods of graphene production, functionalized graphene nanostructures, anticorrosion coatings based on graphene nanostructures and the fundamentals of computer simulation. The literature review also includes such methods of characterization of graphene nanostructures as Raman spectroscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy.

The second section of the thesis presents the computer models of the graphene nanostructures, the calculation of the efficiency of their anticorrosion properties using the "first-principles" methods. This section includes computer simulation and quantum-mechanical numerical calculations of the effectiveness of the anticorrosion properties of graphene, graphene containing defects and graphene coating functionalized with gallium.

The third section presents the methods of graphene production by chemical vapor deposition (CVD) and by carbon diffusion through nickel, functionalization of few-layer graphene nanostructures by gallium ions and graphene oxide production by the modified Hummers' method, after which the electrophoretic deposition of the obtained graphene oxide on the copper and nickel surfaces was carried out. In addition, the results of the study of the effectiveness of protective coatings based on graphene nanostructures by energy dispersive X-ray spectroscopy, as well as numerical calculations of the focusing properties of a new type electrostatic energy analyzers on the base of a conical face-field are presented. When testing a new specialized Auger-analyzer in the work were obtained Auger spectra of the nickel foil after the formation on it anticorrosion protective coatings based on few-layer graphene nanostructures.

The relevance of the study

One of the important constructional, technical and economic problems of our time is the protection of materials and products from the effects of aggressive environmental factors, which include mechanical action, chemical effects of gases and liquids, high temperatures, as well as radiation of various kinds. Such aggressive influences can lead not only to the deterioration of physical and mechanical characteristics, but even to complete destruction. This thesis focuses on the problem of corrosion, which leads to partial or complete destruction of materials as a result of chemical, electrochemical, and physicochemical interaction with the environment. Corrosion of metal products is a widespread problem, especially in industrialized countries with a large number of enterprises, where metal products and equipment are used daily in conditions of aggressive environments, high temperatures and pressures. In the near future the problem of corrosion may become a significant problem of the world economy due to the depletion of world metal reserves and it is necessary to address it now to ensure the safety of the stock of metal products. Based on the above, prediction and prevention of corrosion problems is one of the most important tasks of industry and economy. To solve this problem Nobel Prize winner K.S. Novoselov proposed to use graphene nanostructures as a very effective anticorrosion coating because of their chemical inertness and impermeability.

Ideal defect-free graphene film is capable of becoming ultrathin and effective anticorrosion coating. However, obtaining the graphene film of large size on an industrial scale has certain unresolved technological problems. The difficulties of obtaining the perfect graphene coating can be solved by replacing it with functionalized graphene nanostructures (FGNS), which are much easier to obtain on a large scale and their physical and mechanical properties can be close to those of graphene, which in turn stimulates a huge scientific interest from researchers around the world. Graphene oxide (GO) is one of the most common representatives of FGNS, which can be easily applied to various surfaces, which is a great advantage in coating technologies.

This thesis is devoted to the theoretical and experimental studies of the anticorrosion protective coatings based on graphene nanostructures. A common and optimal method for growing graphene coatings is the chemical vapor deposition (CVD) method, as well as the proposed and implemented method of obtaining graphene by carbon diffusion through nickel. Especially, the graphene grown directly on the surface of copper and nickel by the CVD method has a higher resistance to corrosion in contrast to the transferred graphene. Functionalization of graphene can be carried out by various methods, including oxidation, doping, creation of radiation defects and other methods. There are two main categories of functionalization of graphene: chemical and non-chemical. Both types of functionalization contribute to changing the properties of graphene, but the most effective and cost-effective is the chemical modification.

The detailed study of nanosystems associated with the creation of protective coatings is a difficult task even for well-equipped laboratories. An important method to study and predict the barrier properties of graphene nanostructures is computer simulation and quantum-mechanical numerical calculations. The use of numerical methods such as DFT allows us to obtain sufficiently accurate information about the properties of the studied complex nanosystems and to predict their behavior under different external factors. Computer models of nanomaterials allow researchers to better understand their features and open up new possibilities for functionalizing and modifying their physical, mechanical and chemical properties.

The purpose of the thesis is the theoretical and experimental study of the effectiveness of anticorrosion protective coatings based on graphene nanostructures under the influence of external factors.

The tasks of the thesis:

1. Computer simulation of graphene nanostructures, calculation of the efficiency of their anticorrosion properties using "first-principles" methods;
2. Development of technology for obtaining coatings based on graphene nanostructures on the surface of copper and nickel for corrosion protection;
3. Study of the protection efficiency of the obtained coatings based on graphene nanostructures by energy dispersive X-ray spectroscopy under the influence of various external factors;
4. Development of a specialized Auger analyzer for the analysis of ultrathin layers of anticorrosion protective coatings based on graphene nanostructures.

The objects of the study are protective coatings based on graphene and FGNS.

The subject of the research

Anticorrosion properties of graphene nanostructures under the influence of various external factors.

The methodological basis of the study

Quantum-mechanical numerical methods of the density functional theory, technology for obtaining graphene nanostructures by chemical vapor deposition, obtaining of graphene nanostructures by the diffusion method under vacuum conditions, obtaining graphene oxide films by electrophoretic deposition, analytical methods (optical microscopy, electron microscopy, Raman spectroscopy, Auger electron spectroscopy, energy dispersive X-ray spectroscopy, thermogravimetric analysis, X-ray diffraction).

The scientific novelty of the thesis

1. For the first time, computer simulation and quantum-mechanical numerical calculations of various possible situations were carried out, where graphene nanostructures demonstrate a sufficiently high energy barrier when an oxygen molecule penetrates through them;
2. The method of deposition of graphene oxide film by preliminary heat treatment in a flow tube in a stream of argon-hydrogen mixture (90% Ar + 10% H_2) was improved, which enhanced the adhesive properties and resistance of anticorrosion protective coatings;
3. For the first time was shown high efficiency and reliability of anticorrosion protective coatings based on graphene at temperature exposure using complex methods of materials characterization;

4. For the first time was developed a specialized electrostatic energy analyzer for Auger electron spectroscopy, allowing to analyze ultrathin layers of anticorrosion protective coatings based on graphene nanostructures.

The scientific and practical significance of the study

The obtained results are of both theoretical and practical value. In terms of theoretical value, the computer simulation is of great scientific interest, since it is able to predict and evaluate the anticorrosion protective properties of graphene nanostructures at the nanoscale, which is difficult to achieve in real laboratory conditions. It is well known that today computer simulation is an indispensable tool for solving a wide range of problems in physics and chemistry, including the study of corrosion processes.

The simulation results predict the high efficiency of the protective properties of the anticorrosion coatings based on graphene nanostructures. Moreover, the experimental results obtained in the course of the work are in good agreement with the quantum-mechanical calculations, which is of great practical interest for industrial, shipbuilding, oil and gas and other companies that incur huge annual losses when dealing with corrosion-related problems.

During the thesis work for a more accurate quantitative analysis of the composition and structure of graphene's thin layers, a specialized Auger analyzer was developed and this method of analysis was implemented in the ultrahigh vacuum unit USU-4, due to which the sensitive analysis to light elements of thin near-surface layers of various materials became possible.

The main provisions for the defense of the thesis

1. Ideal graphene, graphenes with structural defects in the form of vacancy, divacancy and a small gap in the sheet (0.25 nm) have a high efficiency of protective effect against oxygen penetration due to the formation of a potential barrier when the oxygen molecule interacts with the surface of the graphene layer.

2. In the graphene sheet with sufficiently large gaps (0.45 nm) the maintenance of high efficiency of protective effect against oxygen penetration is achieved by its functionalization with impurity gallium atoms due to the formation of a strong Ga-C covalent bond (2.6 eV) and high oxygen adsorption energy of gallium (1.8 eV).

3. Anticorrosion graphene coatings obtained by chemical vapor deposition demonstrate reliable protection of copper and nickel surfaces from thermal corrosion, which is associated with the high quality of the coatings (D/G ratio ≈ 0.08).

4. Auger spectrometer, designed and implemented using the Conical Face-Field Electrostatic Energy Analyzer ($R_E \approx 0.71$ % for $\gamma = -0.04$ and $R_E \approx 0.60$ % for $\gamma=0$), allows to control both small and large areas of anticorrosion graphene coatings, as well as their structures in situ.

The author's personal contribution

Computer models and theoretical calculations were carried out by the author using the DFT method in Dmol3 module of the Materials Studio program.

Experimental studies of the anticorrosion protective coatings based on graphene nanostructures, namely, obtaining, processing and analysis of the results were performed independently. Author also completed a scientific internship from June 15 to September 15, 2019 under the guidance of Dr. G.W. Beall at Texas State University in San Marcos, Texas, USA.

Publications

Based on the thesis materials 11 publications were made, including 3 articles published in journals recommended by the Committee for Control of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, 1 article was published in the “Journal of Electron Spectroscopy and Related Phenomena” in 2022, which is included in Scopus database (percentile: 60%), 2 articles published in 2019 in the “Journal of Computational and Theoretical Nanoscience” included in Scopus database, 1 article in international journal “Journal of Materials Science and Engineering B” and 4 abstracts published at national and international conferences.

Relation of the dissertation topic with the plans of scientific works

This dissertation work was carried out within the scientific project № AP05130413 "Development of technology for creating protective coatings based on functionalized graphene nanostructures and researching their properties" funded under the grant funding for scientific and (or) scientific and technical projects of the Committee of Science of the Ministry of Education and Science of Kazakhstan.

Volume and structure of the thesis

The thesis contains a list of symbols and abbreviations, an introduction, the main part of 3 sections, a conclusion and a list of references. The work is presented on 102 pages, contains 69 figures, 5 tables and 232 bibliographical references.