**ABSTRACT**
**of the thesis for the degree of Doctor of Philosophy (Ph.D.)**
in specialty «8D07112 – Nanomaterials and nanotechnologies»

**SULTANGAZINA MARZHAN NURLANQYZY**

# FEATURES OF PLASMA-CHEMICAL SYNTHESIS IN THE LIQUID PHASE OF FERROMAGNETIC NANOPARTICLES IMMOBILIZED IN A CARBON MATRIX

**General characteristics of the work:** The dissertation is devoted to experimental studies aimed at obtaining ferromagnetic nanoparticles immobilized within a carbon matrix by the plasma-chemical synthesis method in a liquid medium**.**

**Relevance of the research:** The development of nanotechnology has significantly influenced the advancement of synthesis methods for functional nanoparticles, with particular attention given to ferromagnetic nanoparticles. Due to their unique magnetic, physicochemical, and structural properties, these particles have found wide application in biomedicine, photocatalysis, data storage systems, energy technologies, and modern electronic devices.

Ferromagnetic nanoparticles based on transition metals such as iron, nickel, and cobalt (Fe, Ni, Co) exhibit enhanced magnetic properties compared to their bulk counterparts or oxide forms. However, their synthesis is associated with a number of technological challenges, including the tendency of nanoparticles to undergo surface oxidation, corrosion, and agglomeration. To preserve their metallic state and prevent agglomeration, various methods of immobilizing nanoparticles within protective coatings are employed.

One of the most promising approaches to addressing this challenge is the immobilization of nanoparticles within protective coatings, with carbon-based structures demonstrating high thermal and chemical stability, mechanical strength, and the capability to form ordered carbon shells. Existing immobilization strategies include the deposition of coatings onto pre-synthesized nanoparticles (e.g., via chemical vapor deposition, CVD), as well as the in-situ formation of a shell during synthesis, as implemented in laser ablation techniques. However, both approaches are constrained by scaling limitations and the considerable technological complexity of the overall process.

A distinctive feature of the electric discharge method in a liquid medium is the possibility of one-step, rapid, and environmentally clean synthesis of metallic nanoparticles immobilized within a carbon matrix. The components required for the formation of nanostructures are supplied by both the electrodes themselves and the liquid medium, enabling the immobilization of nanoparticles using metallic electrodes made of transition metals (Fe, Ni, Co) or graphite electrodes in combination with carbon-containing liquids.

Plasma-chemical synthesis in the liquid phase represents an innovative approach to the production of functional nanomaterials. Plasma generation using an arc electrical discharge ensures high energy efficiency of the process and promotes

reactions under extreme conditions favorable for the formation of stable carbon shells. The method is characterized by high selectivity and a high degree of immobilization, enabling the controlled formation of nanostructures with a specified composition.

Of particular significance is the ability to synthesize carbon shells containing complex magnetic phases such as Fe–Co and Co–Ni, which expand the functional properties of the resulting nanoparticles and make this method especially promising for applications in magnetic, catalytic, and biomedical technologies.

The set of advantages inherent to plasma-chemical synthesis in a liquid medium determines its scientific and practical significance. Conducting experimental studies on nanoparticle immobilization using this method not only contributes to the development of approaches for synthesizing multifunctional materials but also deepens the understanding of the fundamental aspects of plasma–liquid interactions. This, in turn, opens new technological prospects, including wastewater treatment and the production of clean hydrogen.

**The aim of the dissertation** is to conduct an experimental study of the synthesis of ferromagnetic nickel and iron nanoparticles immobilized within a carbon matrix using plasma-chemical synthesis in liquid dielectric media, as well as to investigate their morphological, structural, and magnetic properties.

**The object of the research** comprises ferromagnetic nanoparticles immobilized within a carbon matrix, as well as the plasma-chemical synthesis method in a liquid medium employing various types of liquids and electrodes.

**The subject of the research** is the synthesis of ferromagnetic nanoparticles immobilized within a carbon matrix by the plasma-chemical method in a liquid medium, specifically in distilled water and carbon-containing liquids (alcohol, toluene).

To achieve the stated aim, the following **objectives** were set:

1. Determination of the optimal conditions for the synthesis of ferromagnetic nanoparticles immobilized within a carbon shell by the electric arc discharge method in a liquid medium.
2. Investigation of the morphology and structure of the carbon shell of the synthesized nanoparticles in distilled water, alcohol, and toluene.
3. Study of the magnetic properties of pure ferromagnetic nanoparticles and those immobilized within a carbon shell.

**Research Methods.**

To achieve the objective of the work and to accomplish the tasks set, the following research methods were employed for the study of the synthesized immobilized nanoparticles: methods for analyzing particle size and structure using analytical equipment such as a scanning electron microscope (Quanta 3D200i SEM FEI), an optical microscope (DM 6000M, Leica), and a transmission electron microscope (TEM, JEOL JEM-1400 Plus); as well as structural characterization methods, including Raman spectroscopy using a spectrometer of inelastic light scattering (Solver Spectrum, NT-MDT, laser wavelength 473 nm).

**Scientific Novelty of the Work**

1. The regularities governing the formation of immobilized metal–oxide–carbon nanocomposites synthesized by arc plasma-chemical processing in deionized water have been established for the first time. It has been demonstrated that nickel and iron form stable spherical particles with different degrees of metallic phase retention and product yield, while the increase in the graphitization of the carbon matrix is directly related to the discharge conditions and the nature of the metal.

2. The structural features of nickel and iron particles synthesized in carbon-containing media (alcohol and toluene) have been identified. It has been shown for the first time that toluene as a liquid medium promotes the formation of stable Ni–C and Fe–C nanocomposites.

3. Differences in the magnetic characteristics of Ni–C and Fe–C nanocomposites upon heating have been established. Furthermore, for the first time, the experimental Curie temperatures of ferromagnetic particles immobilized within a carbon matrix have been obtained and compared with theoretical models based on cohesive energy.

**The main results of the study obtained and established during the dissertation work:**

1. The formation of immobilized metal–oxide–carbon nanocomposites based on nickel and iron, produced by arc plasma-chemical synthesis in deionized water, is accompanied by the generation of spherical particles with sizes of 250–300 nm (Ni) and 29–115 nm (Fe). Nickel retains the dominance of the metallic FCC phase with a pure Ni content of 56.8 at. %, whereas iron-containing structures demonstrate a significantly higher mass yield of 0.08 g/min compared to 0.027 g/min for nickel. Concurrently, the reduction of the $I_D/I_G$ ratio to 0.33–0.45 for Ni and 0.34–0.47 for Fe indicates an increased degree of graphitization and the formation of a more ordered carbon matrix in the synthesized composites.

2. Plasma-chemical synthesis in alcohol and toluene carbon-containing liquid media leads to the formation of immobilized nickel and iron nanoparticles with distinct structural features. In alcohol, nickel forms particles of approximately 0.28 μm, which after annealing exhibit a combination of FCC and HCP phases, while iron produces smaller spherical nanoparticles of about 0.06 μm containing $Fe_3O_4$ oxide phases. In toluene, nickel is synthesized as particles of about 0.11 μm with transient formation of $Ni_3C$ carbide and a highly graphitized carbon matrix, whereas iron yields partially carbon-encapsulated cores of 10–20 nm dominated by low-oxidized FeO and metallic α-Fe phases.

**Theoretical and Practical Significance of the Research**

The results obtained in the present dissertation possess both fundamental and applied value and are of interest to the international scientific community in the fields of plasma physics, materials science, nanotechnology, chemistry, and electronics. The development and experimental validation of a single-stage, technologically simplified, and economically efficient method for synthesizing ferromagnetic nanoparticles immobilized within a carbon matrix enables significant reductions in the cost of producing functional nanomaterials with predetermined morphology and properties.

The practical significance of the work lies in the potential application of the obtained transition-metal-based nanoparticles (Fe, Ni, Co) in a number of high-technology fields. Among these are catalytic processes, in which these nanoparticles may serve as alternatives to expensive noble-metal-based catalysts, as well as biomedical technologies, including non-invasive bioimaging, photodynamic therapy, and the targeted delivery of pharmaceutical agents and genetic material.

The theoretical significance of the research lies in the investigation of the mechanisms of growth and formation of ferromagnetic nanoparticles under plasma-chemical synthesis conditions in a liquid medium, as well as in identifying the influence of arc discharge parameters and plasma properties on the morphology and physicochemical characteristics of the synthesized nanomaterials. The analysis of these processes contributes to a deeper understanding of plasma–liquid interactions and expands current knowledge of the fundamental regularities governing the formation of carbon nanostructures that immobilize the particles.

The necessity of conducting such research at the national level is driven by the broad range of potential applications of the obtained results, including in fields that are strategically important for Kazakhstan, such as energy, electronics, nanotechnology, and plasma technologies. Of particular significance are the carbon nanomaterials obtained through the proposed approach, which may serve as model systems for studying nanoscale magnetic phenomena, the interaction processes between nanoparticles and the carbon matrix, and the influence of immobilization on magnetic and electronic properties.

**The reliability and validity** of the results obtained are confirmed by the experimental data acquired during the execution of the dissertation work. In addition, their credibility is supported by publications in high–impact factor international journals and in the proceedings of international scientific conferences held both abroad and within the region.

**Author's Personal Contribution**

The synthesis of the obtained nanoparticles and the investigation of their properties were carried out independently by the author. The formulation of the research objectives and the discussion of the experimental results were conducted jointly with the academic supervisors.

**Publications**

Based on the materials of the dissertation, five publications have been issued in journals indexed in the Scopus and Web of Knowledge databases, along with nine conference abstracts published in national and international scientific conferences.

**Approbation of the Dissertation Work.** The results obtained were reported and discussed at the following international conferences: «XVI International Conference Hydrogen Materials Science and Chemistry of Carbon Nanomaterials (ICHMS'2019), Kyiv, 2019», «18th series of Advanced Energy Materials conference ( 6-8 April,2022, Imperial College London)», «Xth Annual Conference of the Nanotechnology Society of Russia (2020)», IV International Conference "Functional Materials for Innovative Energy (FMIE-2023)", Kyiv, Ukraine.International Scientific Conference of Students and Young Scientists "Farabi Álemi", Almaty, Kazakhstan, April 6–8, 2022.International Scientific

Conference of Students and Young Scientists “Farabi Álemi”, Almaty, Kazakhstan, April 6–9, 2019.International Satpayev Readings “Innovative Technologies as the Key to Successful Solutions of Fundamental and Applied Problems in the Mining and Oil & Gas Sectors of the Economy of the Republic of Kazakhstan”, Almaty, Kazakhstan, April 2019.International Scientific Conference of Students and Young Scientists “Farabi Álemi”, Almaty, Kazakhstan, April 6–9, 2024.

**Relevance of the dissertation topic to research plans**

The dissertation was carried out in accordance with the research plans of Project No. AP09260730 “Hydrogen Generation Based on Composite Nanoparticles Obtained by the Plasma-Chemical Method.”

**Scope and structure of the dissertation**

The dissertation includes a list of abbreviations and symbols, an introduction, a main body consisting of three chapters, a conclusion, and a list of references. The work comprises 106 pages, 51 figures, 8 tables, and 180 bibliographic references.