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DEVELOPMENT OF RESEARCH OF LOW-DIMENSION METAL-CONTAINING SYSTEMS FROM P.P. WEYMARN TO OUR DAYS

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The article analyzes main laws discovered by P.P.Weymarn (1879-1935) during his work at the Saint-Petersburg Mining University, they are connected with obtaining metal-containing disperse substances with nanometer particle size. It enlists priority papers in this field (1906-1915) and describes peculiarities of P.P.Weymarn scientific school which has several connections to modern research being conducted at the Saint-Petersburg Mining University in the field of «nanotechnology» as well as by foreign scientists. The paper reveals continuity in the field of several objects (disperse metals) and the methodology of studying the properties and stoichiometry of substances depending on dispersity. It provides information on achievements in synthesis of surface nanostructured metals and low-dimension forms of substances in various porous matrixes.

Among the studies of the XXI century developing Weymarn's ideas there can be noted solid-state hydride synthesis of metals, layering of different-sized molecules of ammonium compounds on metals (Al, Cu, Ni, Fe), as well as synthesis of metal nanostructures (Ag, Cu, Bi) using porous glass as a particle size stabilizing matrix. In the latter case, the dispersity of the metal increases while its melting point decreases.

***Key words*:** nanophysics and nanomaterials, nanotechnology of metals, low-dimensional state of matter, P.P.Weymarn, V.B.Aleskovsky

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Introduction. Low-dimensional systems including nanofilms, nanoparticles of substances, «wires» with nanometer diameter (e.g., carbon nanotubes), are being widely used in science and technology and are of great interest for development of new metallurgical and additive technologies. Therefore, the Saint-Petersburg Mining University organizes annual academic symposiums «Nanophysics and nanomaterials» aimed at development of nanotechnology and introduction of low-dimensional systems [8].

The founder of nanotechnology science is the alumni and professor of the Saint-Petersburg Mining Institute (now a university) Petr Petrovich Weymarn [9], who in 1906-1916 fulfilled pioneering work in the field of low-dimensional systems.

This paper is aimed at analyzing the research trends in the field of low-dimensional systems based on metals, considering the results of P.P.Weymarn's papers and recent Russian and foreign publications.

Research methods are analytical, comparative, historical, and textual.

Results and discussion. Until 2012, many researchers of Weymarn's works mistakenly believed that he had discovered colloid chemistry [10, 16] (in fact it was done by T.Graham in 1862), and his achievements were associated primarily with this science. In fact, P.Weymarn's ideas were not confined by colloid chemistry only. He initiated the creation of new science called «dispersoidology», which studied the properties of surfaces and processes occurring in them [2]. The field of science, which P.Weymarn called dispersoidology, in our opinion, is closest to chemistry and physics of dispersed substances surfaces. Today, it is almost obvious that this area is the fundamental principle of nanotechnology.

Let us systematize the main achievements of P.Weymarn during his work at the Saint-Petersburg Mining University (1908-1915):

• He found out that between the world of molecules and microscopically visible particles there is a special type of substance with a range of new physicochemical properties – ultra-disperse or colloidal state formed at particle size of 10^{-5}-10^{-9} m at which films have thickness, and fibers and particles have diameter in the range of 1-100 nm.

• He stated the basic law of dispersoidology: during physicochemical or mechanical grinding of material, it tends to turn into forms or states with smaller amount of surface energy; these forms and states have lower surface tension and, in the vast majority of cases, lower density [2].

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• He studied over 200 disperse systems and determined that it is possible to create special conditions in them under which substance crystallization or dissolution processes produce highly disperse stable systems (particle size is less than 0.1 μm) [1, 4].

• He established that as the degree of dispersity increases, the electrical resistance of chemically pure metals increases, and the temperature coefficient decreases.

• He formulated the basic ideas and operating principles of electric ultramicroscope, which enabled investigation of opaque substances (metals) [3].

• He also formulated conceptual foundations and methods of modern nanotechnological approach [8, 9].

In the mentioned period P.Weymarn published 26 articles in the journal «Zapiski Gornogo instituta», 17 of them were devoted to the problems of dispersoidology [9]. These articles were the priority ones, they had the abovementioned results. Almost simultaneously or with a small delay in time P.Weymarn sent his works for publication in the scientific journal «Kolloid-Zeitschrift» (Germany), where from 1917 to 1935 he published 211 articles [9, 16]. From 1908 to 1912 P.Weymarn published six monographs some of them were printed in publishing house «Teodor Steinkopff». At that time, the academic circles used German as a language of international communication. Therefore, already by 1916-1920, the work of P.Weymarn became world famous [9, 10, 16]. The Nobel laureate in chemistry W.F. Ostwald called Weymarn a brilliant scientist. In honor of P.P.Weymarn, the Australian mineralogist Felix Korn called the first colloidal mineral weymarnite. The famous Japanese professor K.Kashima noted that the studies conducted by Weymarn in Japan in 1921-1924 characterize him as an outstanding scientist [16]. Some of the results of P.Weymarn's scientific work were successfully used in the Japanese industry [10].

The English version of Wikipedia has an article about Weymarn's law (1906), it says: colloidal dispersions are obtained from very dilute or very concentrated solutions but not from intermediate solutions. The relative supersaturation ratio herein is defined by $S = (Q\text{-}L)/L$ (where Q is the amount of the dissolved material and L is its solubility. Weymarn's law underlies sol-gel technologies, which are among methods of modern nanotechnology.

Weymarn studied under Academician N.S.Kurnakov and professor I.F.Shreder, who was the head of the Mining Institute from 1912 to 1918. In 1902 while being a student, Weymarn published his first scientific work in co-authorship with N.S.Kurnakov. Later Weymarn rarely published articles in co-authorship with students. The exception was his assistant I.B. Kagan [1, 4]. In general, the students of P.Weymarn (I.D. Avalov, S.Ya.Levites, N.I.Morozov, K.D.Lugovkin, B.V.Byzov, A.Yanek, etc.) helped him in calculations or carried out auxiliary experiments. Weymarn performed key experiments and wrote articles by himself. After his assistants finished their internship, P.P.Weymarn allowed them to work and publish papers independently.

One of the most gifted students, A.M.Yanek, without co-authors published in Saint-Petersburg the book «Dispersoidology» (1915). N.V.Khisamutdinova writes with reference to P.Weymarn's colleagues that he established his scientific school, consisting of talented students, who were successfully developing the ideas of his teacher [10]. Despite the revolution, the Civil War (1917-1921), the students continued to develop the ideas of P.Weymarn. Some of them (K.D.Lugovkin, N.I.Morozov, A.M.Yanek), together with Weymarn moved to work first in Ekaterinburg, at the Ural Mining Institute (1917-1919), then at the Vladivostok Polytechnic Institute (1919-1921).

Thus, there is evidence that P.P.Weymarn created a scientific school. There is continuity of generations, world recognition of results, general scientific direction of activity, stability of scientific reputation, training of highly qualified personnel. P.P.Weymarn continued the tradition of scientific school of physicochemists of the Saint-Petersburg Mining Institute (G.I.Gess, N.S.Kurnakov, I.F.Shreder). The objects of research of this school (e.g., metals) and the peculiarities of methodology were used by P.Weymarn and are still being used in current activities conducted at the Saint-Petersburg Mining University [9], in particular, in the works of direct followers of V.B.Aleskovsky, they currently work at the university and actively research dispersed metals and

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the relation of properties and dispersity of solids [7, 9, 26, 27]. The noted scientific and methodological features are also characteristic of several of Weymarn publications [1-4]. In the XXI century the trend for researching dispersed metal particles, often found in a matrix of porous glass or silica (carbon) materials, as well as size effects in the properties of the resulting metal-substrate systems, is typical for the work of many Russian [5, 6, 21, 22] and foreign researchers [11, 14, 20, 28].

The results of studying graphene fragments of shungite carbon, original nanoscale hybrid fillers for polymers, and obtaining carbon nanoparticles by sublimation are demonstrated in [17, 23]. N.N.Rozhkova reported on the change in the structure of shungite carbon in the temperature range of 1500-2000-2950 °C [23]. X-ray diffraction analysis and Raman spectroscopy confirmed that thermally treated carbon nanoparticles are characterized by a high degree of structural ordering.

A recently published study [18] contains computer simulation data on the behavior of C_{44} carbon nanoparticles when heated in an inert atmosphere of argon. The reaction equilibrium constants, which are possible in the carbon-argon system, are determined, and graphs of the dependence of these constants on temperature are constructed. The results of studying the properties of fullerenes and nanocarbon are relevant for the creation of new alloys and «smart» composites [17, 23].

The results of a study of the effect of steel with a ferrite-cementite-type structure on the kinetics of the anodic dissolution process are discussed in [24]. In particular, the role of interphase (ferrite/ ferrite) and intergranular (ferrite/cementite) boundaries on the initiation of anodic dissolution has been established. It is interesting that part of the research was carried out in the laboratories of the Novolipetsk metallurgical plant.

A study [12] performed at the Saint-Petersburg Mining University presents data on the strengthening and metalling of layered graphite materials with lithium ions during electrochemical interaction. By using various physical methods, it is established that the filling of cavities in layered graphite occurs because of formation of intercalation compounds during surface ionization.

The paper [13] has interesting results on structure and application of powders with micron and nanoscale particles obtained by iodine transport method. In the study conducted under supervision of S.P.Bogdanov, the possibilities of using this method for creation of protective coatings on steel were analyzed [15].

Based on the carried-out analysis and taking into account the works of P.P.Weymarn and papers about him cited in this article and in [9], we can note the following:

• Professor of the Saint-Petersburg Mining Institute Petr Petrovich Weymarn, who conducted pioneer research in the field of nanotechnology, formulated laws, conditions and a method for obtaining colloidal solutions with a controlled dispersity of the solid phase (up to molecular) more than 100 years ago (1906-1915).

• In the process of studying the electrical resistance of disperse pure metals, P.Weymarn proposed the basic ideas and operating principles of an electric ultramicroscope having particle size measuring accuracy up to several nanometers.

• The first publications dealing with dispersoidology and obtaining nanoscale particles were published in «Zapiski Gornogo instituta».

• The first scientific work was published jointly with N.S.Kurnakov (one of the founders of the metallurgy school at the Mining Institute) in the journal of the Russian Physical-Chemical Society.

• P.P.Weymarn continued and developed the traditions of the famous scientific school of physicochemists of the Mining Institute under the leadership of Academician N.S.Kurnakov and managed to create his own scientific school in the field of dispersoidology (physics and chemistry of the dispersed substances surface), which underlies modern nanotechnology. The peculiarity of this school is that it, in fact, was international, as P.Weymarn actively worked with researchers from German universities (Wolfgang Ostwald and others), and in 1921-1935 with Japanese graduate students [9, 10, 16].

• The objects and methodology of research done by Professor Weymarn in the field of low-dimensional metals are continued in modern academic publications, including papers from the Saint-Petersburg Mining University. Among the promising studies of the XXI century based on Weymarn's ideas we can single out the following: solid-state hydride synthesis (SSHS) of surface-

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nanostructured dispersed metals, layering of different-sized molecules on metals (Al, Cu, Ni, Fe) [7, 9, 24-26], as well as the synthesis of metal nanostructures using porous glass as a stabilizing particle size matrix [5, 6]. In the study of the low-dimensional forms of Ag, Cu, and Bi, the authors of papers [5, 6, 28] confirm that P.P.Weymarn's proposition that as the dispersity of the metal increases, its melting point decreases [2, 3].

• The preparation of nanostructured metallic materials by the SSHS method, or by chemisorption of ammonium and organosilicon compounds on metals, performed in an open direct-flow system (off from equilibrium) made it possible to experimentally confirm the reproducibility of composition and compliance of composition constancy low for solid synthesis products [25, 26].

Let us state facts indicating that over 100 years ago P.Weymarn had a point of view compliant with modern views developed by scientific school of V.B.Aleskovsky [19]. Both Alaskovsky and Weymarn contrary to Kurnakov's and other authors vies on the long-discussed issue of constancy of composition of chemical compounds (solids) agreed that the law of composition constancy for these substances must be fulfilled. Weymarn wrote back in 1912 that «dispersoideology can solve the famous dispute between Proust and Berthollet, which deeply touches issues of general chemistry, and show that Berthollet was far from reality, arguing that chemical compounds can occur in all relations» [2, p. 130]. Discussing types, nature and possibility of adsorption compounds dissociation, Weymarn argued that «this should not give rise to the recognition of a special class of chemical compounds, compounds of variable composition» [1, p. 90]. V.B.Aleskovsky independently concluded that «the very concept of» compound variable composition «contains a clear contradiction» [19, p. 755], since the same chemical compound cannot have a different chemical composition. According to the ideas developed by the Alaskovsky school, it is necessary to obtain nanolayers and nanoparticles of constant composition under conditions of irreversible chemical synthesis (for example, by molecular layering [19] or by solid-state hydride synthesis [7, 25, 26]).

For the last 100 years, the tools and methods for studying low-dimensional structures have developed significantly. Nanoobjects are now studied in dozens of methods, including using XPS and EDX-spectroscopy, EXAFS, STM, AFM, neutron and electron diffraction, SIMS. In all fairness we must say that Weymarn used the most advanced methods (at the beginning of the 20th century), for example, Zygmondi ultramicroscope [1, 3, 4]. The description of progress in the field of instrumentation for nanotechnology research is not the main goal of this work. Therefore, we will summarize the main milestones of study of low-dimensional states of matter, primarily from the point of view of relevance and applicability of synthesized solid materials, as well as the shift in their research objects.

Main conclusions. The analysis of works devoted to low-dimensional systems, starting from the research of P. Weymarn, allows us to distinguish the following trends:

• Several studies have appeared (on molecular layering, solid-state hydride synthesis of metals, etc.), which justify the fulfillment of the law of composition constancy – the basic law of stoichiometry of substances - for low-dimensional systems, which is important for the reproducibility of syntheses during industrial use. In the publications of the XXI century considerable attention is paid not only to metal, but also to carbon materials (fullerenes, carbon nanotubes, shungite, graphene).

• In practice composite materials are even in higher demand. They can be built based on the same carbon or ceramic materials used as matrix-substrate, intercalated in their structure by nanofilms or metal nanoparticles or their compounds, for example oxides.

• In the beginning of XX century P.P.Weymarn investigated methods of obtaining and properties of various highly disperse substances: sulfates, chlorides, metals. In the XXI century considerable attention is paid to problems of surface stabilization and properties of low-dimensional substances, which expands the possibilities of their use. This is evidenced by publications in leading world scientific journals and the results of the work of international symposiums on the problems of studying and using nanostructured materials.

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