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Д.В. Сокольский атындағы «Жанармай,
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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
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NEWS

OF THE ACADEMY OF SCIENCES
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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

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**FORMATION OF NANO-AND ULTRAFINE
PALLADIUM POWDERS IN THE PRESENCE
OF «RED-OX»SYSTEM«TITANIUM (III) - TITANIUM (IV)»**

Abstract. The results of studies on the processes of obtaining ultra - and nanodispersed palladium powders from sulphate solutions by a combined chemical and electrochemical method in the presence of a "red-ox" system of titanium (III) - titanium (IV) are presented. It has been shown that when a titanium trivalent sulphate solution is added to a solution containing palladium (II) ions, palladium ions are immediately reduced to elemental state to form a nanodispersed powder. The completeness of the above-mentioned oxidizing-reducing reactions is established on the basis of calculating the equilibrium constant (K), which is 10^{34} and indicates that trivalent titanium ions completely reduce palladium ions to elemental state.

Effect of initial concentration of palladium ions on amount of formed palladium powder with addition of equivalent amount of trivalent titanium ions is investigated.

According to the authors, upon reduction of palladium ions, elemental palladium is formed in the atomic state, and over time, the atoms begin to combine with each other. Subsequently, atomic particles are combined into colloidal particles. It has been found that in the absence of coagulants, the colloidal palladium solution is stable for 2-3 hours, and in the presence of gelatin, the stability increases and remains for 36 hours.

It was shown that in all experiments powders with spherical particles are formed, the average sizes of which range from 0.116-0.240 microns.

Based on the results of the presented studies, a new technology for producing ultra - and nano-sized palladium powders is proposed.

Keywords: ultra-dispersed nanosized powders, palladium, titanium(III) ions, "red-ox" system, reduction, dispersion.

Introduction. Palladium is known to have special physical and chemical properties such as high corrosion resistance, heat resistance, mechanical strength, hardness, high catalytic activity and unique hydrogen sorption properties. In addition, palladium is much cheaper than other platinum metals. It is also known that the application of palladium on the contact surfaces significantly increases the service life of various radio and electrical equipment [1].

Palladium powder has been shown to have very high catalytic activity [2].

In the modern world, many industries, including machine-building, are developing in the direction of creating low-waste and waste-free technologies. Cutting of metals, which is one of the main methods of making parts, is economically disadvantageous because up to 60% of metal is lost.

The main method for making parts from metals, including parts of a complex configuration, is powder metallurgy, which allows to reduce the amount of waste by more than 10%.

The intensive development of modern technology for the production of non-ferrous, rare and noble metals requires the involvement of new modern methods. In recent years, much attention

has been paid to the development and implementation of various non-reactive electrochemical processes, which is due to their significant capabilities in chemical, metallurgical and other remodeling.

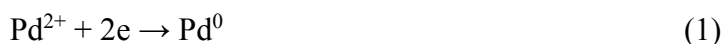
Technologies of electrochemical extraction of metals, synthesis of their various compounds, as well as production of ultradisperse and nano-sized powders used in various industries and national economy are constantly developing.

The interest of many authors in metal powders is caused by the fact that in the modern world the demand for ultradisperse powders with nano-sized particles is growing. While previously palladium powder was used mainly only in the manufacture of the article, the scope of its application is now expanding more and more. One promising direction is the use of nanomaterials in the basis of the technology of creating new drugs, including those having wound healing effect [3-6]. It was found that when entering living organisms, nano-sized metal particles cause a biological response different from the action of the traditional ionic form of elements. It has been shown that nanoparticles of d-elements with parenteral administration are 7-50 times less toxic than metals in ionic form. Nanoparticles easily penetrate all organs and tissues and have a prolonged effect. In biotic doses, they stimulate metabolic processes and exhibit multifunctional effects.

There are data [4] that Acticoat, Nucryst brand dressings, which include silver nanoparticles, are widely used in the USA for the treatment of wounds, burns, trophic ulcers, eczema, acne rash. At the same time, in the practice of treating wounds of different etiologies, there remains a high need for soft dosage forms. In this regard, attention is drawn to the creation of metal nanoparticles, in particular palladium nanoparticles, which can serve as one of the components of soft dosage forms. The function of palladium in the body is well studied and its absolute need is proved at all stages of the process.

The antibacterial effect of certain metals and their compounds has been known since ancient times [2]. The study of the biological activity of copper and palladium nanoparticles, which differ in dispersion and phase composition to create a soft dosage form, is devoted to many studies conducted with the participation of medical workers. The dispersion of metal powders is a very important characteristic of them and in recent years the industry needs fine and nano-sized powders.

Experimental. Previously, palladium powders were prepared using chemical reducing agents such as hydrazine, formaldehyde and hydrogen, reduced with zinc, magnesium, as well as other metals having a more negative potential. An electrochemical method for producing palladium powders is also known. For example, [8] shows the possibility of cathodic deposition of palladium black from palladium (II) chloride solutions at certain pH values of the solution. From a palladium chloride solution at high cathode current densities at the cathode, palladium (II) ions are reduced to form palladium powders by the reaction:



The purpose of our work is to develop a new method for producing ultra-dispersed palladium powders in the presence of titanium (IV) ions. The objective of the study is to identify the conditions and regularities of the process of producing ultra-dispersed and nanosized palladium powders by chemical and electrochemical methods in the presence of the "red-ox" system of titanium (III) - titanium (IV).

The tests were carried out in a 50 ml thermostat cell at room temperature. To the sulphate solution containing palladium (II) ions was poured a titanium trivalent sulphate solution. At the same time, almost immediately palladium ions are reduced to elemental state with formation of metal powder by reaction:



It should be noted that by mixing solutions containing palladium (II) and titanium (III) ions in an equivalent ratio under certain conditions for ten seconds, the solution becomes colorless (note that the initial solution of titanium trivalent sulfate is violet and chloride palladium is reddish), i.e. clear. We presumably explain this phenomenon by the fact that at this moment palladium is in an atomic state, due to the very small particle sizes it becomes practically invisible.

After 2-3 minutes, palladium atoms begin to combine (group) with each other to a certain state, forming agglomerates in which the particle sizes depend on the experimental conditions. Further, colloidal particles of dark-colored palladium are formed throughout the volume of the solution, the stability depends on the conditions of the experiment. In the absence of coagulants, the colloidal palladium solutions remain stable for 2-3 hours and in the presence of gelatin for 36 hours.

In all experiments, powders with spherical particles are formed, the average sizes of which range from 0.116-0.240 microns. Figures 1a and b show micrographs of powders obtained from palladium chloride solution at different concentrations of palladium (II) ions. Micrographs obtained using an electron microscope.

Effect of initial concentration of palladium (II) ions on amount of formed palladium powders with addition of equivalent amount of trivalent titanium ions by reaction (2) was investigated. Table 1 shows the amount of palladium powder formed from the palladium chloride solution - 2 g/l, sulfuric acid - 100 g/l and with the addition of an equivalent amount of titanium (III) sulfate.

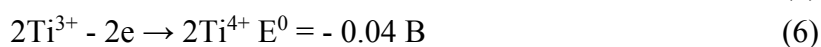
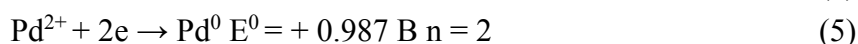
Table 1 - Influence initial concentrations of ions of palladium (II) on the mass of powder of palladium (V = 25 ml)

Palladium ion concentration, g/l	Weight of palladium in solution, mg	Weight of formed palladium powder, mg
0,25	6,25	6,0
0,50	12,50	12,2
0,75	18,75	18,5
1,00	25,00	24,1
1,25	31,25	30,9
1,50	37,50	37,0

As can be seen from Table 1, the reaction (2) is completely shifted to the right, the palladium ions contained in the solution are almost completely reduced to elemental state as ultradisperse powders. Palladium powder yield above 96%.

The completeness of the redox reaction in the reaction of the above two "red-ox" pairs is easily determined by calculating its equilibrium constant according to the known formula [9]. Reactions that are substantially complete must have a constant greater than 10^8 (with 99.99% of the starting materials being bound). To calculate the equilibrium constant of any reversible "red-ox" reaction, it is necessary to calculate $\lg K$ using the formula $\frac{n(E_1^0 - E_2^0)}{0,059} = \lg K_{\text{red-ox}}$, and then K :

$$K_{\text{red-ox}} = 10^{\frac{(E_1^0 - E_2^0)n}{0,059}} \quad (3)$$



$$\lg K_{\text{Pd}^{2+}/\text{Ti}^{3+}} = \frac{(E_1^0 - E_2^0)n}{0,059} = \frac{2(0.987 + 0.04)}{0,059} = \frac{2 \cdot 1.027}{0,059} = \frac{2.054}{0,059} = 34.8 \quad (7)$$

Equilibrium constant $K \cong 10^{34,8}$

The value of the constant of the above redox systems, equal to $K = 10^{34.8}$, suggests that both reactions go to the end from left to right and are practically irreversible. In addition, since the reaction constant represents the ratio of the product of the concentration of the final reaction products to the product of the concentrations of the starting products, the equilibrium of the above reaction occurs when $[2\text{Ti}^{3+}]^2 * [\text{Pd}(\text{II})]$ becomes more than $[\text{Ti}^{4+}]^2 * [\text{Pd}]$ by 10^{34} times.

The results of our calculations show that trivalent titanium ions are completely spent on reducing palladium (II) ions to elemental state.

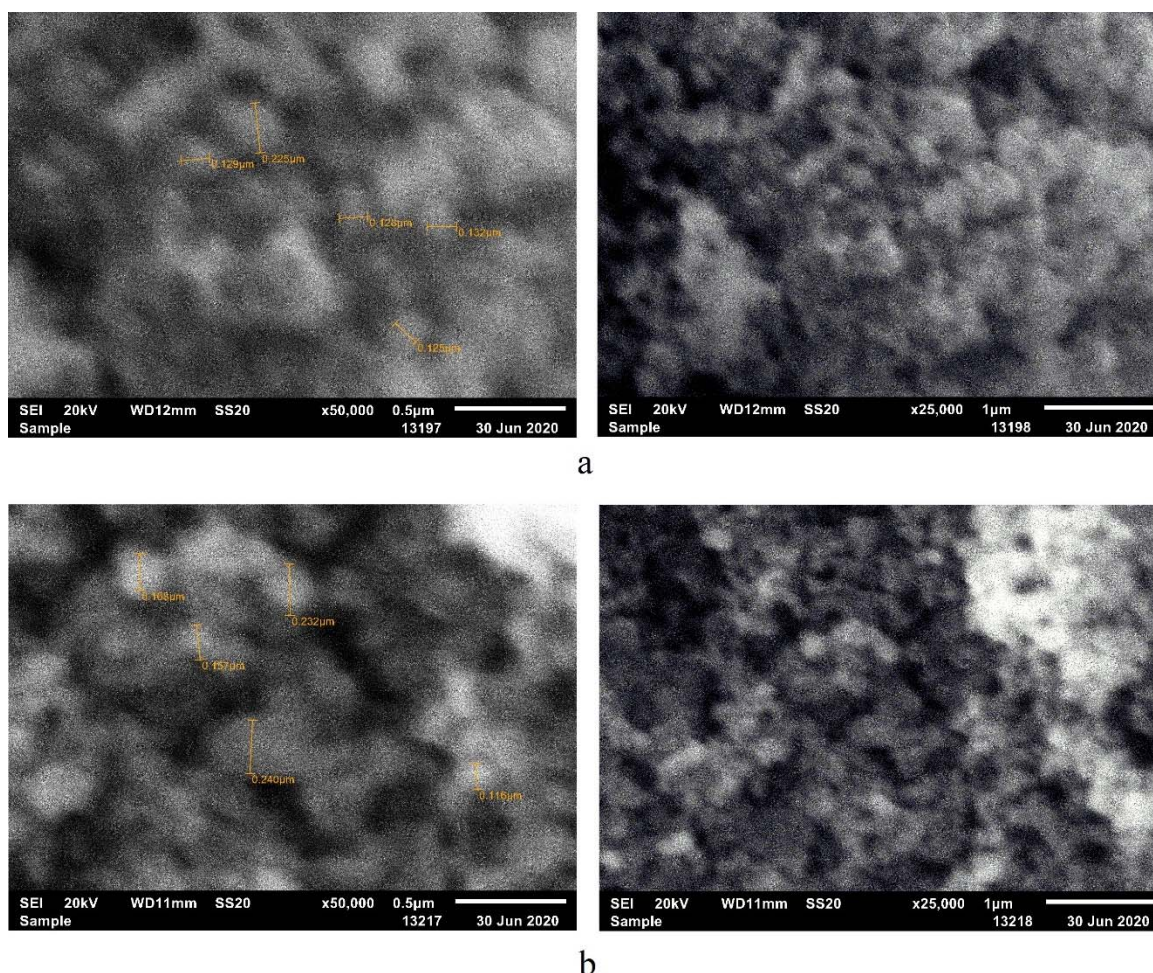


Figure 1 - Electron microscopic photographs of palladium powders obtained by reduction with titanium (III) ions:
 a - at initial content of palladium (II) ions - 0.1 g/l; b - at initial content of palladium (II) ions - 0.05 g/l

Based on the results of laboratory studies, we have proposed a new technological scheme for the production of ultra-dispersed palladium powders (figure 2).

We have previously shown [10-12] that in acidic solutions, when titanium electrodes are polarized by industrial alternating current under certain conditions, they are intensively dissolved to form trivalent ions colored purple. In carrying out such experiments, we have discovered a new phenomenon, which consists in the fact that after preliminary polarization of titanium electrodes with non-stationary currents, their further self-dissolution takes place in sulphate and hydrochloric acid solutions with the formation of titanium (III) sulfate and chloride, respectively. In this connection, it is very easy to obtain titanium trivalent salts. As can be seen from figure 2, by polarizing titanium electrodes (2) with industrial alternating current at a frequency of 50 Hz, titanium (III) ions are obtained in the electrolysis cell (1). In the reactor (2), a solution of titanium (III) sulfate was added to the palladium (II) chloride solution while stirring. In this case,

elemental palladium is formed in the form of powder with particles of nanoscale values. In an electrolysis cell (3) in which the electrode spaces are separated by an anionite membrane, titanium (IV) ions are reduced in the cathode space to a trivalent state.

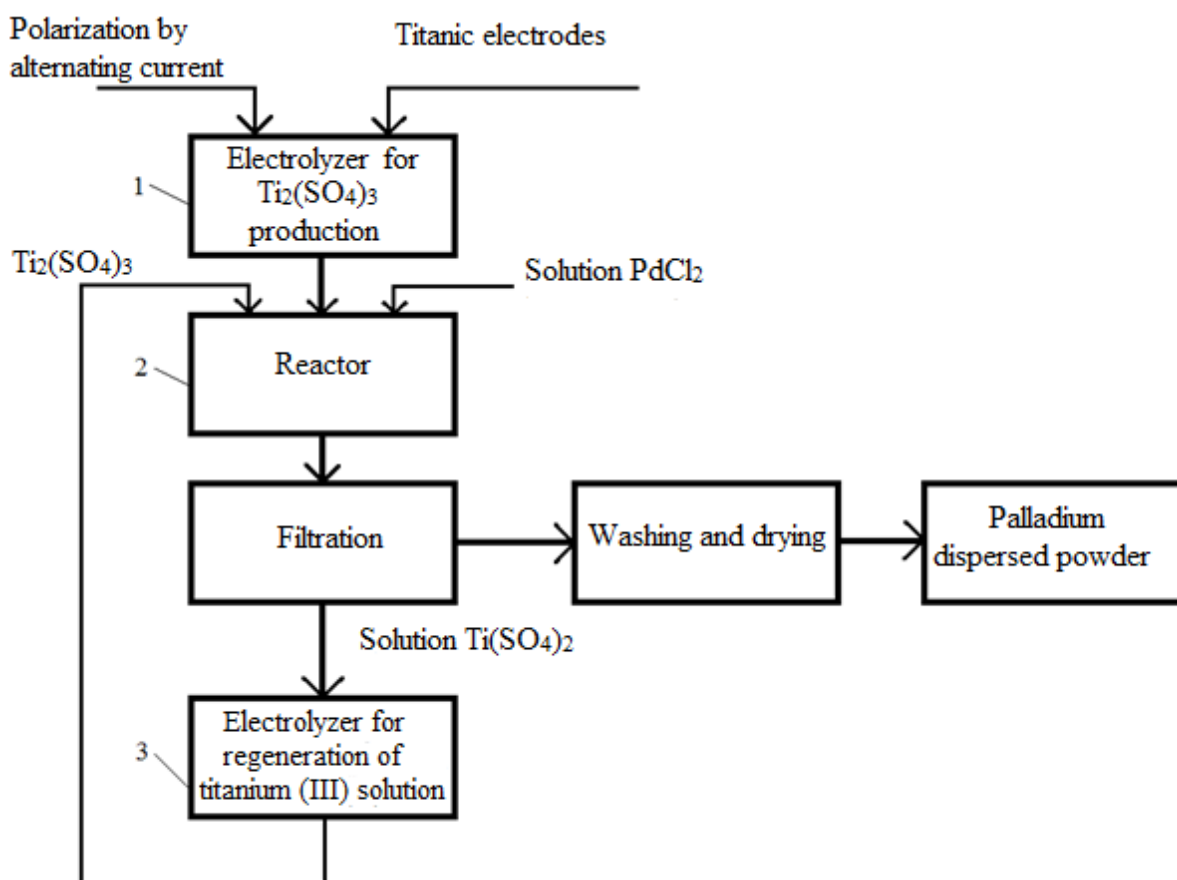


Figure 2 - Process flow diagram of production of ultra-dispersed palladium powders at cementation of palladium (II) ions with trivalent titanium ions: 1 - electrolyzer with titanium electrodes; 2 is a reactor for producing ultra-dispersed palladium powders; 3 shows an electrolytic cell with anionite membrane-separated electrode spaces for regeneration of titanium trivalent.

Palladium powders are separated by filtration, washed until there are no impurity ions, dried. All these processes are carried out in a box filled with inert gas (for example, carbon dioxide or argon). The obtained powder is placed in a sealed container.

When palladium powders are formed by reaction (1), trivalent titanium is converted to a quadrivalent state. Formed sulphate solution of tetravalent titanium is fed into cathode space (3) of electrolysis cell, in which electrode spaces are separated by anionite membrane. Titanium (IV) ions are reduced to trivalent state. A solution containing titanium (III) ions is sent to reactor (2) and reaction (1) is carried out again in this reactor to obtain palladium powder.

Thus, earlier we first showed the possibility of producing ultra - and nano-sized copper powders in the cathode, prianodic, as well as in interelectrode spaces [13-15], and in this work we first showed the possibility of producing nano- and ultradisperse palladium powders in the presence of the red-ox system "titanium (III) - titanium (IV)." On the basis of the conducted laboratory studies, a process scheme for producing ultra-dispersed palladium powders is proposed. It is shown that by this technology palladium powders of spherical shape with particle size 0.116 - 0.240 mcm are formed.

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НАНО- ЖӘНЕ УЛЬТРАДИСПЕРСТІ ПАЛЛАДИЙ ҰНТАҒЫНЫҢ «ТИТАН (III) – ТИТАН (IV)» RED-OX-ЖҮЙЕСІ ҚАТЫСЫНДА ТҮЗІЛУ

Аннотация. Мақалада ультрадисперсті және наноөлшемдегі палладий ұнтағын «титан (III) – титан (IV) «red-ox» жүйесінің қатысында алудың біріктірілген химиялық және электрохимиялық әдісін жасауға арналған зерттеулер нәтижелері келтірілген.

Тәжірибелер бөлме температурасында көлемі 50 мл-ге тең термостатталған ұяшықта жүргізілді. Құрамында палладий (II) иондары бар күкіртқышқылды ерітіндіге үшвалентті титанның күкіртқышқылды ерітіндісі қосылды. Осы кезде палладий иондары бірден наноөлшемді ұнтақ түрінде элементті күйге дейін тотықсызданады.

Құрамында палладий (II) және титан (III) иондары бар ерітінділерді эквиваленттік арақатынаста белгілі жағдайда араластырған кезде он секунд ішінде ерітінді түссізденетіні, басқаша айтқанда, мөлдір болатыны анықталды (үшвалентті титан сульфатының ерітіндісі бастапқыда күлгін түсті, ал палладий хлоридінің түсі – қызыл). Бұл құбылыс былайша түсіндіріледі: бұл кезде палладий атомарлы күйде болады және бөлшек өлшемі өте кіші болғандықтан, көзге көрінбейді. 2-3 минуттан соң палладий атомдары құрамындағы бөлшек өлшемі тәжірибе жағдайына тәуелді болып келетін агломераттар түзе, белгілі бір күйге дейін бір-бірімен біріге (топтала) бастайды. Осыдан соң ерітіндінің бүкіл көлемінде палладийдің қоңыр түсті коллоидты бөлшектері түзіледі, олардың тұрақтылығы тәжірибе жағдайына тәуелді болып келеді. Коагулянттар жоқ болған кезде коллоидты палладий ерітінділері 2-3 сағат бойы тұрақты болады, ал желатин қосылғанда олар 36 сағат бойы тұрақты күйінде сақталады.

Электрондық микроскоп арқылы палладий (II) иондарының әртүрлі бастапқы концентрацияларында алынған ұнтақ микросуреттері түсірілді. Барлық тәжірибе нәтижесінде бөлшектері сфера тәріздес, орташа өлшемі 0,116-0,240 мкм аралығында ұнтақ түзілетіні анықталды.

Үшвалентті титан иондарын эквивалентті мөлшерде қосқанда палладий (II) иондарының бастапқы концентрациясының түзілетін палладий ұнтақ мөлшеріне әсері зерттелді. Бұл кезде палладий (II) иондарының бастапқы мөлшерінің 96%-тен астамы ультрадисперсті ұнтақ түрінде элементті күйге өтетіні анықталды.

Палладий және титан иондарының әрекеттесуі кезінде тотығу-тотықсыздану реакциясының толық өтуі «red-ox» жүйенің реакция константасын есептеу арқылы анықталды. Аталған тотығу-тотықсыздану жүйесі константасының шамасы $K \approx 10^{34}$ және бұл шама екі реакцияның екеуі де солдан оңға қарай толық жүретінін және іс жүзінде қайтымсыздығын болжаудың негізі болып саналады. Жүргізілген есептеу нәтижелері үшвалентті титан иондарының палладий (II) иондарын толық элементті күйге дейін тотықсыздануына жұмсалатынын көрсетті.

Жүргізілген лабораториялық зерттеулер негізінде палладийдің ультрадисперсті ұнтағын алудың жаңа технологиясының принципіалды сызба-нұсқасы ұсынылды. Сонымен қатар, мақалада тотықсыздандырғыш үшвалентті титан сульфатын алу жөнінде деректер келтірілген. Алынған деректер титан электродтарын қышқылды ерітінділерде өндірістік айнымалы токпен поляризациялау арқылы белгілі жағдайда палладий (II) иондарын тотықсыздандыратын үшвалентті титан иондарын түзе еритіні көрсетілді.

Түйін сөздер: ультрадисперсті наноөлшемді ұнтақтар, палладий, титан (III), иондар, «red-ox» жүйе, тотықсыздану, дисперстілік.

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ФОРМИРОВАНИЕ НАНО- И УЛЬТРАДИСПЕРСНЫХ ПОРОШКОВ ПАЛЛАДИЯ В ПРИСУТСТВИИ «RED-OX» СИСТЕМЫ «ТИТАН (III) – ТИТАН (IV)»

Аннотация. В статье приведены результаты исследований, посвященных разработке способа получения ультрадисперсных и наноразмерных порошков палладия комбинированным химическим и электрохимическим способом в присутствии «red-ox» системы «титан (III) – титан (IV)».

Опыты проводились в термостатированной ячейке емкостью 50 мл при комнатной температуре. К сернистому раствору, содержащему ионы палладия (II), добавляли сернистый раствор трехвалентного титана. При этом практически сразу же происходит восстановление ионов палладия до элементного состояния в виде наноразмерных порошков.

Установлено, что при смешивании раствора, содержащего ионы палладия (II) и титана (III) в эквивалентном соотношении при определенных условиях, в течение десяти секунд раствор становится бесцветным (исходный раствор сульфата трехвалентного титана имеет фиолетовый цвет, а хлорид палладия – красноватый цвет), т.е. прозрачным. Это явление мы предположительно объясняем тем, что в этот момент палладий находится в атомарном состоянии и из-за очень мелких размеров частиц становится практически невидимым. Показано, что

после 2-3 минут атомы палладия начинают объединяться (группироваться) друг с другом до определенного состояния, образуя агломераты, в которых размеры частиц зависят от условий опыта. Далее, по всему объему раствора образуются коллоидные частицы палладия темноватого цвета, устойчивость зависит от условий опыта. В отсутствие коагулянтов коллоидные палладиевые растворы остаются устойчивыми в течение 2-3 часов, а в присутствии желатина – в течение 36 часов.

С помощью электронного микроскопа сняты микрофотографии порошков, полученных при разных исходных концентрации ионов палладия (II). Установлено, что во всех опытах формируются порошки с частицами сферической формы, средние размеры которых колеблются в пределах 0,116–0,240 мкм.

Исследовано влияние исходной концентрации ионов палладия (II) на количество образовавшихся порошков палладия при добавлении эквивалентного количества ионов трехвалентного титана. При этом более 96% исходного количества ионов палладия (II) переходит в элементное состояние в виде ультрадисперсного порошка.

Полноту протекания окислительно-восстановительной реакции при взаимодействии ионов палладия с ионами титана определили на основе расчета константы реакции «red-ox» системы. Величина константы вышеуказанных окислительно-восстановительных систем, равная $K \cong 10^{34}$, дает основание предположить, что обе реакции идут до конца слева направо и являются практически необратимыми. Результаты проведенных расчетов показывают, что ионы трехвалентного титана полностью расходуется на восстановление ионов палладия (II) до элементного состояния.

На основе проведенных лабораторных исследований предложена принципиально новая технологическая схема получения ультрадисперсных порошков палладия. В статье также приводятся данные о получении восстановителя – сульфата трехвалентного титана.

Приведенные данные показывают, что в кислых растворах при поляризации титановых электродов промышленным переменным током в определенных условиях они интенсивно растворяются с образованием трехвалентных ионов титана, являющихся восстановителем ионов палладия (II).

Ключевые слова: ультрадисперсные наноразмерные порошки, палладий, ионы титана (III), «red-ox» система, восстановление, дисперсность.

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