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**OPTIMIZATION OF THE TECHNOLOGY
FOR THE PRODUCTION OF AMMONIUM TETRAVATE
FOR THE PRODUCTION OF NANOCRYSTALLINE
VANADIUM DIOXIDE**

К.В. Лускань, О.П. Мисов, О.П. Клименко. Оптимізація технології одержання амоній тетраванадату для отримання нанокристалічного діоксиду ванадію. Досліджено вплив технологічних параметрів синтезу амоній тетраванадату на розмір частинок кінцевого продукту діоксиду ванадію. Нанорозмірний діоксид ванадію дозволяє створити необхідні в сучасній електронній техніці електронні елементи у вигляді перемикачів напруги і критичних терморезисторів, параметри яких у декілька разів перевищуватимуть показники подібних елементів. Метою експериментальних досліджень є оптимізація технології одержання амоній тетраванадату для отримання нанокристалічного діоксиду ванадію. Сіль амоній тетраванадату отримували відновленням пентаоксиду ванадію водним розчином щавлевої кислоти з наступним його осадженням розчином лугу, видаленням, промивкою, сушкою осаду в нейтральній атмосфері аргону. Висушену сіль амоній тетраванадата термічно обробляли при температурі 850...900 °С в інертному атмосфері аргону з витримкою 10 хв. Електронною мікроскопією та рентгенофазовим аналізом досліджено вплив технологічних параметрів синтезу амоній тетраванадату на фізико-хімічні властивості VO₂. В результаті синтезу амоній тетраванадату встановлено вплив початкової концентрації V₂O₅ у водному розчині щавлевої кислоти, природи та концентрації лугу у якості осаджувача внесеного до реакційної зони розчину на розмір часток кінцевого продукту діоксиду ванадію. Отримані результати вказують на можливість керування розміру частинок VO₂ зміною технологічних параметрів синтезу амоній тетраванадату. Встановлено, що після термічної обробки при температурі вище 850...900 °С амоній тетраванадат перетворюється на нанокристалічний діоксид ванадію з характерним йому фазовим переходом напівпровідник-метал при температурі 68 °С. Визначено у результаті дослідження була оптимізована технологія одержання амоній тетраванадату для отримання нанокристалічного діоксиду ванадію зі стабільними характеристиками в процесі термоциклування.

Ключові слова: діоксид ванадію, амоній тетраванадат, синтез, фазовий перехід напівпровідник-метал

K. Luskan, O. Musov, O. Klimenko. Optimization of the technology for the production of ammonium tetravate to obtain the nanocrystalline vanadium dioxide. The article is devoted to the influence of technological parameters of the synthesis of ammonium tetravanadate on the size of the particles of the final product of vanadium dioxide. Nanosized vanadium dioxide allows you to create the electronic elements required in modern electronic technology in the form of voltage switches and critical thermistors, which parameters will exceed several times the performance of such elements. The purpose of experimental research is to optimize the technology for the production of ammonium tetravate to obtain the nanocrystalline vanadium dioxide. The ammonium salt of tetravanadate was prepared by the restoration of vanadium pentoxide with an aqueous solution of oxalic acid, followed by precipitating it with a solution of alkali, removing, washing, drying the precipitate in a neutral atmosphere of argon. The dried salt of tetravanadate ammonium was heat treated at a temperature of 850...900 °C in an inert atmosphere of argon with an exposure of 10 minutes. The electron microscopy and X-ray diffraction analysis investigated the influence of technological parameters of the synthesis of ammonium tetravanadate on the physical and chemical properties of VO₂. As a result of the synthesis of tetravanadate ammonium, the effect of the initial concentration of V₂O₅ in the aqueous solution of oxalic acid, the nature and concentration of alkali as a precipitant introduced into the reaction zone of the solution on the size of the particles of the final product of vanadium dioxide was established. The obtained results indicate the possibility of controlling the size of VO₂ particles by changing the technological parameters of the synthesis of ammonium tetravanadium. It was found that after thermal treatment at a temperature above 850...900 °C, ammonium tetravanadate is converted to nanocrystalline vanadium dioxide with a characteristic phase transition of its semiconductor metal at a temperature of 68 °C. Practical value: The result of the study was the optimization of the technology for the production of ammonium tetravanadate to produce nanocrystalline vanadium dioxide with stable characteristics in the process of thermocycling.

Keywords: vanadium dioxide, tetravanadate ammonium, synthesis, phase transition semiconductor metal

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Introduction. Among the common methods for nanocrystals of vanadium dioxide obtaining are: hydrothermal method, molecular stratification method, sol-gel method, and method of high-temperature decomposition of precursors. The main advantage of the method of high-temperature decomposition of precursors (vanadium salts (IV)) is the possibility of obtaining highly dispersed powders with a high degree of chemical purity.

However, scientific literature does not contain data on the influence of the technological parameters of the synthesis of vanadium salt (IV) on the size of the particles and the phase composition of the final product of vanadium dioxide.

To develop the technology for the production of vanadium dioxide from the salt of vanadium (IV), it is necessary to determine the basic parameters of synthesis of tetravanadate ammonium which have a significant effect on the physical and chemical properties of vanadium dioxide.

An analysis of recent publications and problem statement. Extraordinary properties of vanadium dioxide (VO₂) associated with a change in the crystalline structure of the material at the phase transition of semiconductor-metal (PTSM) [1]. Above $T_c=67$ °C, VO₂ is a metal with tetragonal lattice symmetry; below this temperature there is a semiconductor with monoclinic lattice symmetry. PTSM is very fast, it takes about one nanosecond [2], allowing the use of this property vanadium dioxide in a variety of high-speed electronic devices in optical switches, thermochromic indicators, memory elements, energy-saving coatings for glass, sensor technology [3 – 6]. However, until now, not all possibilities for the practical application of PTSM have been realized, which is due to the low stability of the physical parameters of such materials during multiple switching over the temperature of the phase transition and is due to inadequate study of the physical and chemical processes occurring in these materials under the influence of external factors (temperature, pressure). In connection with this, the creation and research of materials with a phase transition of semiconductor-metal, which would be stable in the process of exploitation, is an actual scientific task.

Studies have shown that this disadvantage can be avoided by reducing the size of crystalline particles of vanadium dioxide. Getting vanadium dioxide with a particle size of 10...100 nm allows you to create the necessary electronic elements in the modern electronic devices in the form of voltage switches and critical thermistors, which parameters will exceed several times the performance of such elements.

The aim of the study is to optimize the technology for the production of ammonium tetravate to obtain the nanocrystalline vanadium dioxide.

Materials and methods of research. Preparation of tetravanadate ammonium salt consists of three main stages [7]: obtaining an aqueous solution of oxyanate (IV) by reducing V₂O₅ by aqueous solution of H₂C₂O₄, precipitation of vanadium salt (IV) by the action of alkaline solution on the solution of oxyanate (IV), removal, washing and drying of the precipitate in a neutral atmosphere of argon. At the final stage of the technology, the dried salt of tetravanadate ammonium was heat treated at a temperature of 850...900 °C in an inert atmosphere of argon with a 10-minute exposure [8].

The pH-metric titration was carried out using a standard pH meter 150 MI.

Investigation of the phase composition of the vanadium (IV) salt and vanadium oxide products was performed by X-ray diffraction analysis.

X-ray diffraction analysis was performed by the DRON-2.0 diffractometer with the use of CuK α radiation ($\lambda=0.15418$ nm) in the mode of 35 kV voltage and current 10 mA.

The morphology of the powders was studied by transducing electron microscopy using a JEM-100 cCX II microscope.

Results of the influence of technological parameters of the synthesis of ammonium tetravanadate on the size of vanadium dioxide particles. The first stage of obtaining an aqueous solution of oxovanadium (IV) by the interaction of vanadium pentoxide with oxalic acid solution is described by equation (1):



In this work, the molar ratio of $V_2O_5:H_2C_2O_4$ reagents was chosen 1:4, 1:5. The high acid concentration is due to the need to maintain a rather low pH (1...2) for dissolving vanadium pentoxide and preventing the transition of cation oxyanate to anionic form.

The diffraction pattern of the thermal decomposition of the solution of oxyanate (IV) in an inert atmosphere of argon at a temperature of 850...900 °C is given in Fig. 1.

As can be seen from Fig. 1, the product of heat treatment of the solution of oxyanate (IV) is a mixture of various phases of vanadium oxides (V_5O_9 , V_2O_3 ,

VO_2). It requires additional steps to improve the properties of the final product of vanadium dioxide. One of these steps is deposition of vanadium salt (IV) by the action of a solution of alkali.

Fig. 2 shows titration curves of 0.20 M solution of oxyanate (IV) 0.46 M NH_4OH , $NaOH$, KOH (curve KOH is identical to $NaOH$ curve).

When potentiometric titration of the aqueous solution of the captive action (IV) by sodium hydroxide and potassium, there are two jumps on the titration curve. In the first point of the equivalence of $pH \sim 4.9$, naturally the strong acid is titrated $n(H^+) = 2 \cdot 0.20 \cdot 5 \cdot 10^{-3} = 2 \cdot 10^{-3}$ mol. Next there is a clouding of the solution and precipitate. At pH 9.9 there is a second leap of titration, with the sediment completely separated from the solution. By the results of the calculation, the amount of OH^- , for the precipitation of vanadate (IV) at the second point of equivalence is $(2.50 \dots 2.65) \cdot 10^{-3}$ mole, that is, the ratio $C(VO^{2+}):C(OH^-) = 1:2.5 = 4:10$. Of all possible reactions between VO_2^+ and OH^- , such a stoichiometric relationship is possible only for the reaction (2):



Thus, the precipitate is identified as $V_4O_9^{2-}$. In the case of formation, for example, $V_2O_5^{2-}$, according to the stoichiometry, the ratio $VO^{2+}:OH^-$ should be 1:3 (2:6). Titration results are well reproducible. They are not dependent on the concentration of reagents and are in the range 2:5...2:5.3.

When titration with a solution of ammonia on the curve, there are two points of equivalence identical to the titration curve with alkali. However, the second jump is slightly lower since NH_4OH is a weak base.

The comparative analysis of the influence of alkalis of various nature on the average size of the particles of the final product of vanadium dioxide showed that the size of the particles increases in a number of sediments with cations: NH_4^+ , Na^+ , K^+ , therefore ammonium hydroxide (equation 3) was chosen as the precipitant of vanadium salt (IV)

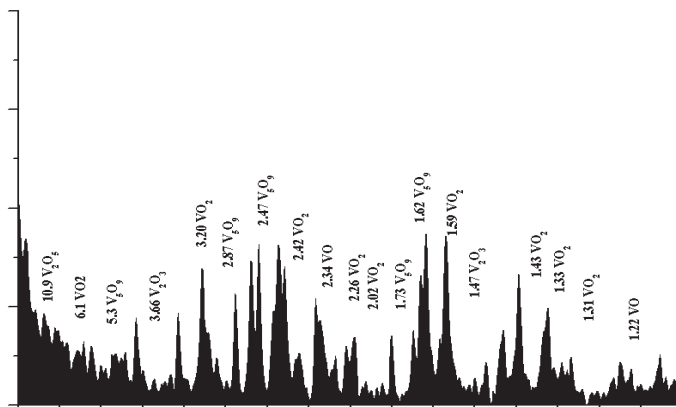


Fig. 1. A diffractogram of a thermally treated solution of oxyanate (IV) in an inert atmosphere at a temperature of 850...900 °C

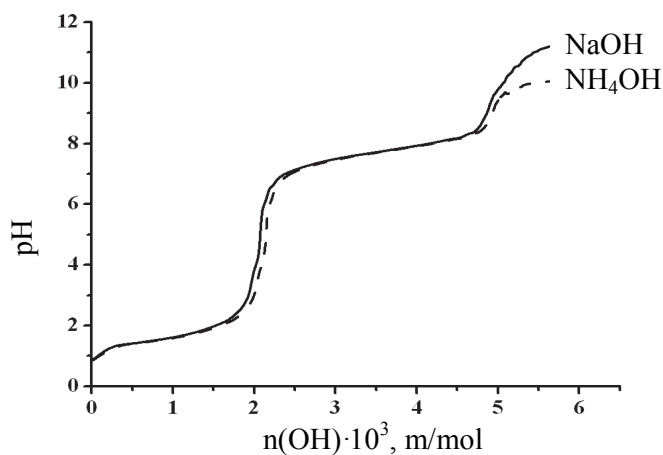
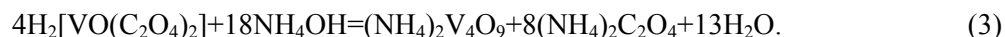


Fig. 2. The potentiometric titration curve of $5 \cdot 10^{-3}$ l of the solution of oxyanate (IV) $H_2[VO(C_2O_4)_2]$ (0.20 mol/L) with NH_4OH , $NaOH$ (0.46 mol/L), 2 °C



To determine the technological parameters that lead to a change in the size of VO_2 particles, experiments have been carried out on the effect of the initial concentration of V_2O_5 at the stage of obtaining an aqueous solution of oxovanadium (IV) (Fig. 3a). In parallel, studies were carried out on the dependence of the scale of VO_2 particles on the concentration of NH_4OH introduced into the reaction zone of oxovanadium (IV) (Fig. 3b). Conclusions regarding the influence of the technological parameters of the synthesis of the salt of vanadium (IV) on the physical and chemical properties of vanadium dioxide were made on the final product VO_2 .

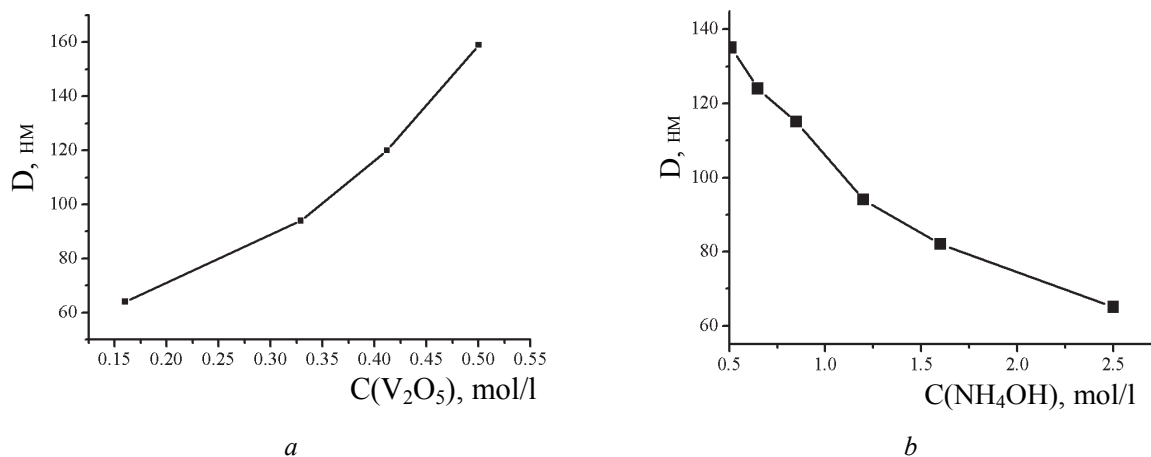


Fig. 3. Influence of the parameters of obtaining tetravanadate ammonium on the size of vanadium dioxide particles: the effect of V_2O_5 concentration on the size of the particles of the final product VO_2 (a); the influence of NH_4OH concentration on the size of the particles of the final product VO_2 , $C(\text{V}_2\text{O}_5)=0.16$ mol/L, $C(\text{H}_2\text{C}_2\text{O}_4)=0.32$ mol/L (b)

As can be seen from Fig. 3a, the concentration of V_2O_5 over 0.3 mol / L leads to obtain VO_2 particles greater than 100 nm, and an increase in the NH_4OH concentration of up to 100 ml of the reaction zone reduces the size of the VO_2 particles to 65 nm. A number of experiments to optimize the production process $(\text{NH}_4)_2\text{V}_4\text{O}_9$ have shown that, depending on the synthesis conditions of ammonium tetravanadate, the size of VO_2 particles can vary from 60...150 nm.

It was established that ultrasonic treatment of the obtained suspension for 1...2 minutes leads to the adherence of particles, most likely associated with an increase in the temperature of the reaction zone at the time of ultrasonic treatment. Consequently, after precipitation of ammonium with a hydroxide, the suspension obtained immediately undergoes the next stage – the separation, and the drying of the precipitate.

To obtain the highest quality target product – vanadium dioxide, the precursor must contain a minimum of compounds of pentavalent vanadium and oxalate ions, which lead to the formation of V_2O_3 . Thus, an important stage in the preparation of precursors is its removal and rinsing.

When choosing methods for removing the precipitate with its subsequent washing, we took into account the ability of the precipitate to be soluble, and to the oxidation of oxygen by air.

The removal of sediment by filtration leads to the oxidation of the salt of vanadium (IV). The best results were obtained by centrifugation with minimizing oxygen deposition of air. The precipitate was separated by a centrifuge with an adjustable speed of 4000 rpm and centrifugation for 10 minutes. Since the water solubility of freshly prepared precipitate of $(\text{NH}_4)_2\text{V}_4\text{O}_9$ depends on pH, to avoid significant loss of tetravanadate ammonium (12~15 %), washing is carried out with 0.05 mol/L ammonium hydroxide solution.

Drying of a precipitate $(\text{NH}_4)_2\text{V}_4\text{O}_9$ in an inert atmosphere at a temperature of 150...180 °C for 3...4 hours is mandatory for salt storage, since the presence of water promotes the rapid oxidation of vanadium to the pentavalent state.

After heat treatment $(\text{NH}_4)_2\text{V}_4\text{O}_9$ at a temperature of 850...900 °C in a neutral atmosphere of argon with a shutter speed of 10 minutes nanocrystalline vanadium dioxide was obtained. This is evidenced by the microphotography (Fig. 4), the diffraction pattern and the expressive endothermic peak at DTA at a temperature of 68 °C, corresponding to the semiconductor–metal transition dioxide vanadium characteristic.

Conclusions. As a result of research, the technology for the production of tetravanadate ammonium, which is a precursor for nanocrystalline vanadium dioxide, has been developed and optimized. The influence of V_2O_5 concentration, the nature of the alkali as a decicing agent, NH_4OH concentration on the size of vanadium dioxide particles and the conditions for removal and washing of the tetravalonate ammonium sediment on the physicochemical properties of vanadium dioxide have been established. It is determined that after thermal treatment at a temperature above 850...900 °C $(\text{NH}_4)_2\text{V}_4\text{O}_9$ it becomes a nanocrystalline vanadium dioxide with a characteristic phase transition of a “semiconductor – metal” at a temperature of 68 °C.

The obtained results indicate the possibility of controlling the size of the particles of synthesized VO_2 during its thermal treatment.

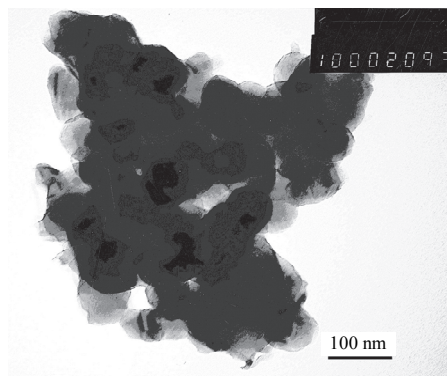


Fig. 4. Micrograph and DTA curve. VO_2 is obtained by thermal decomposing of tetravanadate ammonium at a temperature of 850...900 °C. for 10 min. with a particle size of 80...82 nm

Література

1. Бугаев Л.В., Захарченко Б.П., Чудновский Ф.А. Фазовый переход металл-полупроводник и его применение. Ленинград : Наука, 1979. 183с.
2. Кузнецова Ю.В., Лях О.В., Меркушева Е.В., Сурикова В.И. Диоксид ванадия и твердые растворы на его основе. Фазовые переходы, структура и свойства. Москва, 2013. 104 с.
3. Zhang Z., Gao Y., Luo Z., Solution-based fabrication of vanadium dioxide on F:SnO₂ substrates with largely enhanced thermochromism and low-emissivity for energy-saving applications. *Energy & Environmental Science*, 2011. Vol. 4. P. 4290–4297. DOI:10.1039/C1EE02092G
4. Li W. Zhu J., Liang J. External Electric Field Manipulations on Structural Phase Transition of Vanadium Dioxide Nanoparticles and Its Application in Field Effect Transistor. *The Journal of Physical Chemistry*. 2011. Vol. 115. P. 23558–23563. DOI: 10.1021/jp207196g.
5. Chen S., Ma H., Yi, H., Chen S. Wang Optical switch based on vanadium dioxide thin films. *J.Infrared Physics and Technology*. 2004. Vol. 45. P. 239–242.
6. Пергамент А.Л., Артюхин Д.В., Казакова Е.Л. Физические основы разработки датчиков на основе эффекта переключения в диоксиде ванадия. *Ученые записки Петрозаводского государственного университета*. 2009. №7. С.101–105.
7. Спосіб отримання нанодисперсного порошку тетраванадату амонію: пат. 104512 Україна. № u201506327; заявл. 26.06.2015; надр. 10.02.2016, Бюл №3. 4с.
8. Luskan K.V., Gyrenko O. A., Musov O. P., Klimenko O. P. Influence of the conditions for the preparation and thermal destruction of ammonium tetravanadate on the composition of oxide-vanadic electro-functional materials. *Proceedings of Odessa Polytechnic University*. 2017. 2(52). P. 87–92. DOI: 10.15276/opu.2.52.2017.13.

References

1. Bugaev, L.V., Zakharchennya, B.P., & Chudnovsky, F.A. (1979). *Metal-semiconductor phase transition and its application*. Leningrad: Science.
2. Kuznetsova, Yu.V., Lyakh, O.V., Merkusheva, E.V., & Surikova, V.I. (2013). *Vanadium dioxide and solid solutions based on it. Phase transitions, structure and properties*. Moscow.

3. Zhang, Z., Gao, Y., & Luo, Z. (2011). Solution-based fabrication of vanadium dioxide on F:SnO₂ substrates with largely enhanced thermochromism and low-emissivity for energy-saving applications. *Energy & Environmental Science*, 4, 4290–4297. DOI:10.1039/C1EE02092G.
4. Li, W. Zhu, J., & Liang, J. (2011). External Electric Field Manipulations on Structural Phase Transition of Vanadium Dioxide Nanoparticles and Its Application in Field Effect Transistor *The Journal of Physical Chemistry*, 115, 23558–23563. DOI: 10.1021/jp207196g.
5. Chen, S., Ma, H., Yi., H., & Chen, S. (2004). Wang Optical switch based on vanadium dioxide thin films. *J.Infrared Physics and Technology*, 45, 239–242.
6. Pergament, A.L., Artyukhin, D.V., & Kazakova, E.L. (2009). Physical basis of sensor development based on the switching effect in vanadium dioxide. *Scientific notes of Petrozavodsk State University*, 7, 101–105.
7. Luskan, K.V., Mysov, O.P., & Gyrenko, A.O. (2016). *Method nanodispersed powdered ammonium tetravanadatu*. Ukraine Patent: UA 104512.
8. Luskan, K.V., Gyrenko, O. A., Musov, O. P., & Klimenko, O. P. (2017). Influence of the conditions for the preparation and thermal destruction of ammonium tetravanadate on the composition of oxide-vanadic electro-functional materials. *Proceedings of Odessa Polytechnic University*, 2 (52), 87–92. DOI: 10.15276/opu.2.52.2017.13.

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