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Computer simulation of vanadium dioxide semiconductor phase formation in supersaturated solutions

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Abstract. Modelling the process to obtain vanadium dioxide in systems V – O – H – Na and V – O – H – S has been carried out using the program complex "Selector". The latter is based on a computer method for thermodynamic analysis of equilibrium compositions. The dependences of the concentration of main components in V – O – H – Na and V – O – H – S systems on hydrogen index pH as well as the dependence of the VO₂ concentration on pressure in the system V – O – H – Na are given. The possibility to obtain vanadium dioxide in water solution of the systems involved has been estimated.

Keywords: vanadium dioxide, phase transition, thermodynamical equilibrium, concentration.

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1. Introduction

Below the temperature of $T_k = 68^\circ\text{C}$, crystalline vanadium dioxide (VO₂) is a semiconductor with the forbidden gap width close to 0.7 eV. Above T_k temperature, VO₂ changes into the metallic state due to the 1st order phase transition (PT) "semiconductor – metal" [1]. This transition is accompanied by a jump in all the properties of VO₂. The changes in electrical and optical properties are of special interest for practical applications. Thus, the specific resistivity of monocrystalline vanadium dioxide changes by 10⁴ times within the range of $\sim 3^\circ\text{C}$ around the phase transition temperature. In temperature-sensitive resistors based on VO₂, it gives the temperature coefficient of resistance increase up to $\sim 80\%/K$ at the phase-transition temperatures. These values greatly exceed the corresponding values in available commercial thermoresistors.

PT-induced changes in optical parameters of vanadium dioxide can be applied in photon crystals [2] and in elements of laser optical tracts [3]. It has been found that the phase transition in VO₂ is accomplished within a uniquely short period of time, viz. dozens of femtoseconds [4].

However, the repeated temperature changes over the range that includes the phase transition temperature produce considerable mechanical stresses in the samples, which may result in their cracking. This may shorten the service life of electronic and optical elements based on vanadium dioxide. The results of investigations [5] show that the affects of mechanical stresses on VO₂ sample strengths can be reduced by decreasing geometrical dimensions of vanadium dioxide crystals to the values of less than one micrometer.

The common methods of crystalline vanadium dioxide synthesis provide for producing crystals with minimum averaged dimensions of the order of millimeter units [6]. The most suitable methods for obtaining particles of smaller sizes are the methods of dispersion and condensation [7]. The chemical method for liquid-phase condensation of VO₂ particles in the form of soles is the most acceptable technique for synthesizing vanadium dioxide nanoparticles. Preparation of nanodispersed particles by this method involves the following steps: preparation of a solution of several components possessing rather high solubility, one of them being a vanadium-containing material; initiating a chemical reaction in the solution, which results in producing the required low-soluble vanadium

product; and extraction of the vanadium product from the solution.

The most complicated tasks in the implementation of the above method are: the proper selection of the solution components, the choice of the required technological conditions, the analysis of the chemical composition of the final product, and its decomposition into separate phase components. To practically select the ways of employing this method for an assigned particular product is inexpedient since it requires much effort, cost and time, while the results are unpredictable. The most efficient way to find the proper method of synthesizing a required chemical compound is a computer simulation of phase formation in the solution chosen.

This study is aimed at the development of chemical foundations for the synthesis of nanocrystalline vanadium dioxide by using the condensation method. This involves selecting the initial components and defining the conditions for the most expedient liquid-phase reaction on the base of computer simulation of thermodynamic processes in supersaturated solutions.

To reach the targets, "Selector" software package [8] was used, which is intended to minimize thermodynamic potentials in chemical media.

The software package consists of a system of inter-coordinated databases for thermodynamic data and the bank of initial chemical compositions. "Selector" program medium is based on a coordinated interaction of functional and information block sets. The main of these are: available calculation model database, calculation model creation unit, reference data base, computation unit, computation analysis unit, result presentation unit.

If necessary, the program can form a newly required calculation model in case it is missed from the available model base. The required calculation model is then created using the list of specified allowed equilibrium phases and dependent components, and compositions of independent components.

The program provides several alternative models that differ in thermodynamic potentials used. The program calculations are performed with account of the following six potentials: Helmholtz thermodynamic potential, Gibbs thermodynamic potential, isochoric-isentropic, isobaric-isentropic, isobaric-isenthalpic, and isochoric-isenergetic potentials. The properties of the prototype chemical system determine the choice of an alternative model.

The software package allows calculations of full-, metastable and intermediate chemical equilibrium phase states in systems where aqueous solutions of various electrolytes, gas mixtures, liquid and solid one- and multicomponent phases may be present.

"Selector" program allows estimating the thermal and pressure behavior of the chemical system thermodynamic parameters. Activity coefficients of the aqueous solution components in these systems are estimated using the modified Debye-Huckel equation in the Helgeson version [9]. Calculations are performed

using thermodynamic properties of independent components available in commonly used thermodynamic databases [10, 11].

The productive algorithm of convex programming was used to perform these calculations. The algorithm is based on the method of internal points with one- and two-side restraints on calculation values.

At the final stage of simulations, the calculation result analysis module displays the results in the form of tables; additionally, they may be displayed in a graphic form.

In this study, the "Selector" software package was used to select equilibrium phase states in aqueous vanadium-containing media with the aim of determining chemical conditions for vanadium dioxide phase formation. Two chemical systems were studied: V – O – H – S and V – O – H – Na. Both systems can be implemented in reality as aqueous solutions of vanadium pentoxide with addition of sulfate acid or sodium hydroxide. They were chosen as prototype systems proceeding from good solubility of vanadium pentoxide (V_2O_5) in water (0.07 g vanadium pentoxide is dissolved in 100 g of water at 25 °C). It should be noted that vanadium dioxide is insoluble in water.

The equilibrium phase compositions in the systems involved were obtained by minimization of the Gibbs isobaric-isothermic potential. This appears to be the most reasonable technique, since in this case, the independent thermodynamic parameters would be the temperature and pressure that under real process conditions are set naturally by the environment.

The program calculations of phase formation were performed using dependent components and constituents of the thermodynamic system. The list includes 46 aqueous solution components, 22 gaseous medium components and 22 solid phase components which can potentially take part in the process of creating new phases. The list of solid-phase components includes all vanadium oxides with whole-numbered valence, and most vanadates known so far. The list of aqueous solution components comprises all possible simple vanadium ions and complex ions including tetravalent vanadium ions (oxyvanadyl VO_2^{2+}) and pentavalent vanadium VO_4^{3-} , $H_2VO_4^-$, VO_2^+ and others.

Simulation of phase formation in V – O – H – S system was performed for a virtual chemical medium consisting of vanadium pentoxide V_2O_5 0.055 mol, water 55.5 mol and sulfate acid H_2SO_4 0.25 mol, the sulfate acid content varying from 0 to 0.25 mol by 0.01-mol steps.

The results of the computer simulation of the phase formation in V – O – H – S system indicate that the system produces 11 components, their proportions varying from 10^{-1} to 10^{-18} mol. According to their chemical compositions, the components produced may be separated into two groups: vanadium-containing and sulfur-containing. The first group includes: neutral phases V_2O_5 , H_3VO_4 , anions VO_4^{3-} , $H_2VO_4^-$, HVO_4^{2-}

and cations VO^{2+} , VO_2^+ , VOOH^+ ; the second group comprises SO_4^{2-} and H_2SO_4^- ions. Besides, the thermodynamic system involved includes oxygen O_2 . The ionic state of vanadium differs in vanadium-containing components: V^{5+} (V_2O_5 , H_3VO_4 , VO_2^+ , VO_4^{3-} , HVO_4^{2-}), V^{4+} (VO^{2+}), V^{3+} (VO^+ , VOH^{2+}). It can be seen that the most common components in the V – O – H – S system solution are those with pentavalent vanadium. These are: vanadium pentoxide, orthovanadate acid H_3VO_4 , ions of oxovanadium (V) – VO_2^+ ; their presence in acidic solutions agrees with the available publications [12, 13]. The only trivalent vanadium component is the vanadyl ion VO^{2+} .

The contents for most of solution components depend on the proportion of sulfuric acid in the solution, which determines the solution pH values. Fig. 1 shows the concentrations of the V – O – H – S system main components as a function of the solution pH value at the temperature 25 °C. However, the solution components obtained in concentrations less than 10^{-7} mol/l are not shown in Fig. 1. The range of sulfuric acid contents of the solution, used in the study, provided for the vanadium ion concentration variations from 10^{-4} to 10^{-1} mol/l.

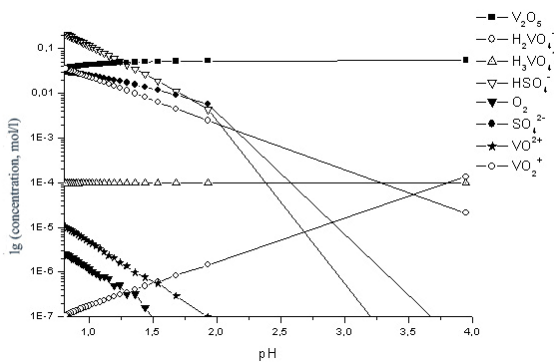


Fig. 1. The concentrations of V-O-H-S system main components plotted against the solution pH value at the temperature 25 °C.

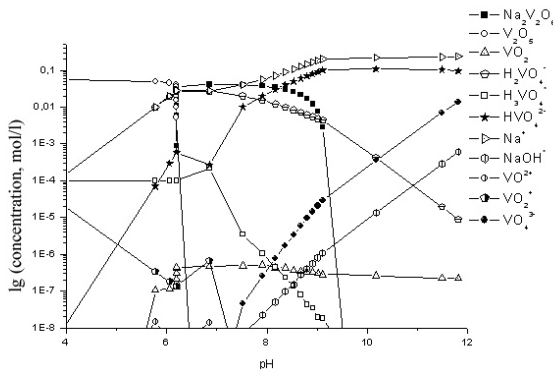


Fig. 2. The concentrations of the V-O-H-Na system main components plotted against the solution pH values at the temperature 25 °C.

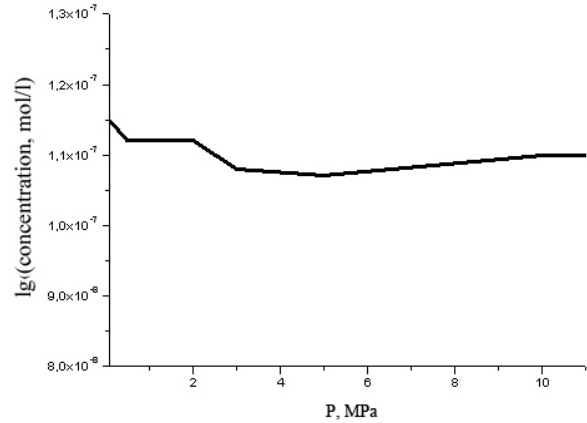


Fig. 3. VO_2 concentrations plotted against pressure in V – O – H – Na system.

The simulation results indicate that the number of components in the prototype thermodynamic system depends on the solution pH value. All the dependences including those in Fig. 1 are monotonic decreasing or increasing functions, their maximum content values being determined by the solution pH value.

Vanadyl ions present in the prototype system (maximum concentration 10^{-2} mol/l) make it perspective for further developments.

The second chemical system used for the simulation of vanadium dioxide phase formation was V – O – H – Na system. For this purpose, the process of vanadium pentoxide interaction with sodium hydroxide (NaOH) in an aqueous solution was simulated. To simulate the phase formation, a virtual medium was used, containing vanadium pentoxide V_2O_5 0.055 mol, water 55.5 mol, and sodium hydroxide varying from 0 to 0.24 mol, in 0.01 mol increments.

The simulation results indicate that the prototype system contains 17 components. These include 7 neutral components: V_2O_5 , NaOH , $\text{Na}_2\text{V}_2\text{O}_6$, H_3VO_4 , VO_2 , O_2 , H_2 ; and 10 ionic components: H_2VO_4^- , HVO_4^{2-} , VOOH^+ , VON^{2+} , VOH^+ , VO^+ , VO^{2+} , VO_2^+ , VO_4^{3-} , Na^+ . The latter, except Na^+ , are vanadium-containing components that contain vanadium in various valent states. Among the neutral components, VO_2 phase is present, which is of special interest for the investigations undertaken.

The component contents of the solution depend on sodium hydroxide content, which determines the pH values in a medium. The solution component concentrations plotted against pH values are shown in Fig. 2. Here, as a simplification, the components obtained in concentrations above 10^{-8} mol/l are only represented. In the representation coordinates used, the functional dependences show different behavior: they may decrease (V_2O_5 , VO^{2+} , VO_2^+ , H_2VO_4^-), increase (NaOH , VO_4^{3-} , Na^+), or reach an extremum ($\text{Na}_2\text{V}_2\text{O}_6$, VO_2 , H_3VO_4 , HVO_4^{2-} , H_2), which is determined by the thermodynamic equilibrium conditions in the system.

The correctness of the performed computer simulation is confirmed by the presence of a well-studied sodium dimethavanadate $\text{Na}_2\text{V}_2\text{O}_6$ [14] in the prototype system, as well as VO^{2+} and VO_2^+ ions characteristic of aqueous solutions of vanadium pentoxide [13], and complex ions of vanadium (V) H_2VO_4^- and HVO_4^{2-} described in [15]. This is also confirmed by the uncharacteristic behavior of the solution pH value that shows its minimum at NaOH content of 0.11 mol. This peculiarity is caused by the concentration dependence maximum formed in the orthovanadate acid H_3VO_4 solution that naturally decreases the pH value. It is significant that the above concentration of sodium hydroxide results in a sharp decrease of V_2O_5 phase content of the solution, which indicates the total vanadium pentoxide dissociation.

The computer simulation results obtained show that VO_2 phase is present in the solution at pH = 6 to 11. Its concentration is practically constant and the maximum content of vanadium dioxide is $5.5 \cdot 10^{-7}$ mol/l and occurs at pH = 7.9. This phase may be most probably present in the form of soles, which allows producing vanadium dioxide in the form of nanoparticles. In the prototype system, these particles may be probably found in an amorphous state, thus an additional thermal treatment may be required for their crystallization [16]. The simulation of thermal and pressure behavior of the vanadium dioxide phase concentrations obtained is important for practical applications. This simulation of VO_2 content dependences on temperature in similar systems indicates that within the temperature range 20 to 100 °C, vanadium dioxide concentrations show a slight increase with temperature [17].

VO_2 content dependences on pressure in V – O – H – Na system, obtained using simulation by means of the “Selector” software package, are shown in Fig. 3. It is obvious that no essential changes of vanadium dioxide content of the solution occur within the range of 0.1 to 10 MPa.

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