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Obtaining and observation of micro- and nano-size V_2O_5 structures

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Simple growing closed-volume technique as similar to the Bridgman method for obtaining of the V_2O_5 micro- and nanocrystalline structures is considered. The morphology features of produced crystalline structures were investigated using scanning electron microscope and X-ray diffraction method. The some observed V_2O_5 structures are briefly described with account of the physicochemical conditions of preparation.

Рассмотрен простой способ получения микро- и нанокристаллических структур на основе V_2O_5 в замкнутом объеме, близкий к методу Бриджмена. С помощью растрового электронного микроскопа и Х-лучевого дифракционного метода исследованы морфологические особенности полученных кристаллических структур. Кратко описаны некоторые наблюдаемые структуры V_2O_5 с учетом физико-химических условий синтеза.

1. Introduction

Vanadium oxides are attracted strong interest material scientists over the past years for their electrical, optical, electrochemical properties: metal-to-insulator transition for most vanadium oxides, electrical switching of V_2O_5, high ion interaction capacity, high sensitivity of active elements for gas sensors etc [1–6]. Vanadium pentoxide in different forms is intensively studied. The nano-compounds V_2O_5 are unique materials with properties which depend on obtaining conditions.

There is a number of recent communications about synthesis of elongated structures based on the V_2O_5. In particular, vanadium pentoxide nanorods and nanowires have been synthesized by reverse micelle technique [2]. The length can be tuned easily by keeping the particles in micellar solution after the synthesis from 40 nm to 1 μm. Authors [3] described a facile method to self-assemble V_2O_5 nanorods into microspheres. In paper [4] it was proposed the synthesis of vanadium pentoxide nanorods based on thermal decomposition of chloride vanadium vapor. The micro- and nanorods with the thickness in the range from 50 nm to 5μm and length up to 7 μm were obtained in the work [4]. The V_2O_5 compacted nanopowder were used by authors [5] and nanorods and nanotips with the thickness in

the range from 50 nm to 100 nm on the top of rods of larger size were got in this case.

In the present study the synthesis of single crystals of V_2O_5 was realized and the conditions of micro- and nano-crystalline formations during growth process of vanadium pentoxide were considered. For this aim we obtained the nominally pure V_2O_5 and with additions (3 and 10 mass. %) of SiO_2 powder. The morphology of micro- and nano-formations in obtained samples was considered. It is note, that it is the first step of V_2O_5 synthesis of single and microcrystals. Our works with the aim to optimize the controlled synthesis regimes are continued.

2. Experimental

Using V_2O_5 powder there were obtained V_2O_5 crystals and elongated micro- and nano-structures with dimension in the range from 0.1 μm to 0.5 μm. Considered structures were from 20 μm to 150 μm maximal length. The investigated nano- and microsize crystalline structures were got in closed volume (silica ampoule). The growing process was based on Bridgman method. The images of the synthesized V_2O_5 structures were obtained by scanning electron microscope (SEM). The phase compositions of the micro- and nano-structures were controlled using the X-ray diffraction (XRD) method.

Our experimental data on growing of nano- and micro-size V_2O_5 crystalline elongated structures were recently reported in [7, 8]. Vanadium oxides have been extensively studied because of their important properties. The V_2O_5 compound has an orthorombic structure with lattice parameters $a = 1.1510$ nm, $b = 0.3563$ nm, $c = 0.4369$ nm [9]. The building block is a deformed octahedron. The shortest V–O bond length corresponds to a double vanadyl bond ($V–O_1 = 0.1585$ nm). The other oxygens are labeled O_2 bonded to two vanadiums, and O_3, bonded to three vanadiums. The longest V–O bond ($V–O_1 = 0.2785$ nm) is a weak van der Waals bond. The V_2O_5 hence has a layer structure with an easily cleavage plane (the *c*-plane).

Vanadium pentoxide has the low melting point (963 K [10]) and crystals obtained easily from the melt. During growing process based on Bridgman technique [11] in this work we obtained the V_2O_5 crystals (Fig. 1) and different structures with micro- and nano-dimensions. V_2O_5 crystals growing was performed in quartz evaquated ampules. The vertical displacement speed was selected about 6 mm/h. Temperature of active zone was higher than the melting temperature per ~30 K. The grown dimensions were cooled to room temperature at the switch off regime of furnace.

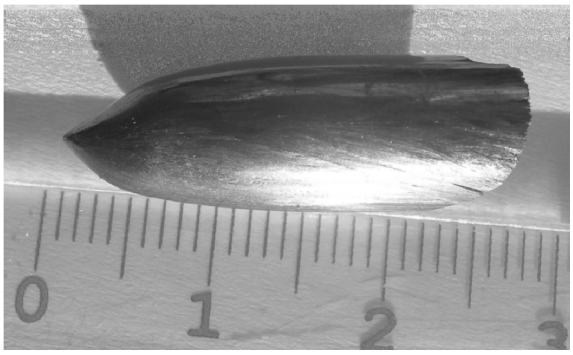

Fig. 1. Photo of a V_2O_5 crystal obtained by the Bridgman method.

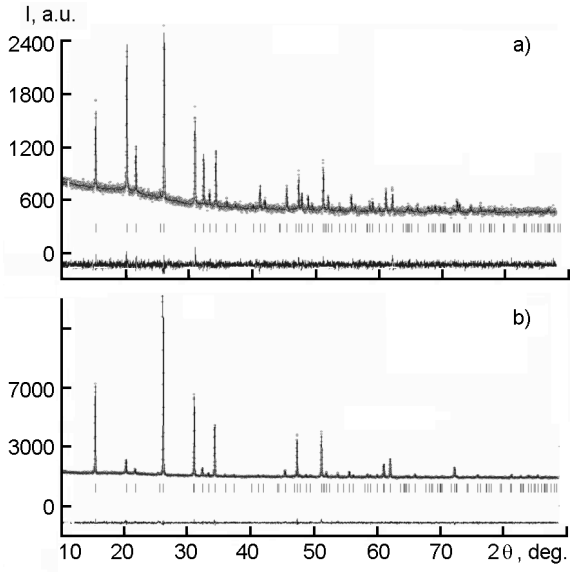

Fig. 2. Typical X-ray patterns of V_2O_5 starting material (a) and grown V_2O_5 nominally pure crystal (b) at 295 K.

V_2O_5 with stoichiometric purity >98.5 % was used as starting material for crystal growth. The non-controlled impurities content was in the range of 0.01–0.30 mass. %. In particular, the Si-compounds contents to average 0.24 mass. %. Before synthesis the starting material was calcined and purified by horizontal floating-zone melting method (thermal treated starting powder). For comparison with standard case (free for special additions) we added to the starting V_2O_5 powder the high disperse SiO_2 (3–10 mass. %). Details about obtained samples are described in the paper [8].

Surface morphology and X-ray microanalysis of the samples were studied using the REMMA-102-02 scanning electron microscope. XRD analysis was performed using a STOE STADI P powder Diffraction System. The arrays of experimental intensities and reflection angles from the investigated patterns were obtained using above mentioned diffractometer with a linear positional sensitive detector PSD upon modified Ghinier geometry scheme, with Bragg-Brentano modes for transmission. Conditions of the measurements were the following: pure $CuK\alpha_1$ radiation ($\lambda = 1.540598$ Å); bent Johan type [111] Ge-monochromator; $2\theta/\omega$-scaning; 2θ-angle range is $4.000° \le 2\theta < =120.000°$; detector's step is $0.480°$ (2θ); step scanned time is 250 s. Others XRD-measurement details were the same as previously described in [12]. The investigations were carried out at room temperature.

3. Results and discussion

A grown V_2O_5 crystal boule is shown in Fig. 1. The obtained crystals are brown or yellow-brown colored, cleave into layers. In crystal bulk the macrodefects (micropores channel) are occasionally observed. The

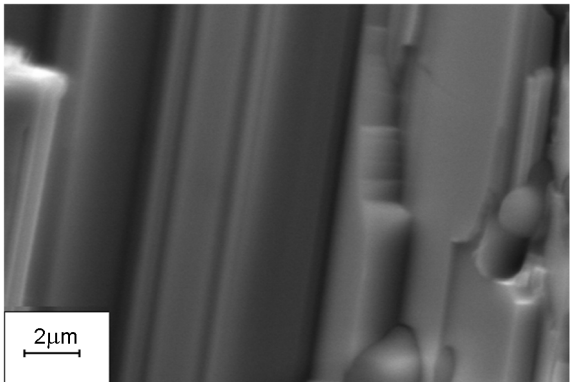

Fig. 3. SEM-image of the V_2O_5 crystalline layers.

XRD-analysis data of starting material and the grown crystal are given in Fig. 2. As shown the XRD-analysis, the obtained crystal is mono-phase. The vanadium pentoxide V_2O_5 crystal structure is belonged to the rombic D^{13}_{2h}–$Pmmn$ space group of V_2O_5 structure type. In the Table 1 the crystallographic characteristics and microstructural parameters of investigate crystals are presented. The coordinates and isotropic thermal parameters in structure are described in the Table 2. The strong texturized surface of samples (the dominated orientation of atomic planes) are observed in

Table 1. The parameters of structure refinement and crystallography data (unit cell parameters (Å) a, b, and c; factors of reliability R_P, R_{WP}, and R_B; average size $<d>$ of coherent dispersion domain, and average maximal stress $<e>$; prevail direction D and parameter δ of orientation) for vanadium oxides. The measurement for starting powder pointed as (I), the sample obtained from thermal non-treated starting powder — (II); sample after thermal treated starting powder during purification by floating-zone method — (III).

V_2O_5	a	b	c	R_P, R_{WP}, R_B, %	$<d>$, Å, $<e>$, %	D, δ
(I)	3.56403(8)	11.5097(3)	4.37164(14)	3.35, 4.22, 5.99	805±36 $14.6(\pm6.5)\cdot10^{-4}$	[110] −0.180(9)
(II)	3.56606(2)	11.51465(10)	4.37678(19)	1.97, 2.54, 4.50	875±209 $12.9(\pm2.7)\cdot10^{-4}$	[001], [110] 2.52(5), 0.575(8)
(III)	3.56542(3)	11.51230(10)	4.3777(2)	2.56, 3.21, 3.57	907±211 $12.5(\pm2.7)\cdot10^{-4}$	[001], [110] 2.26(5), 0.73(2)

Table 2. Positional (x, y, z) and thermal parameters (B_{iso}) of atoms in V_2O_5 structure for the sample III (see Table 1)

Atom	Position	x	y	z	B_{iso}, (Å)^2
V	4e	1/4	0.0963(3)	0.399(1)	0.84(8)
O_1	4e	1/4	0.118(1)	0.068(5)	0.6(3)
O_2	4e	1/4	0.5694(5)	0.536(3)	2.9(2)
O_3	2a	1/4	1/4	0.522(5)	0.7(20)

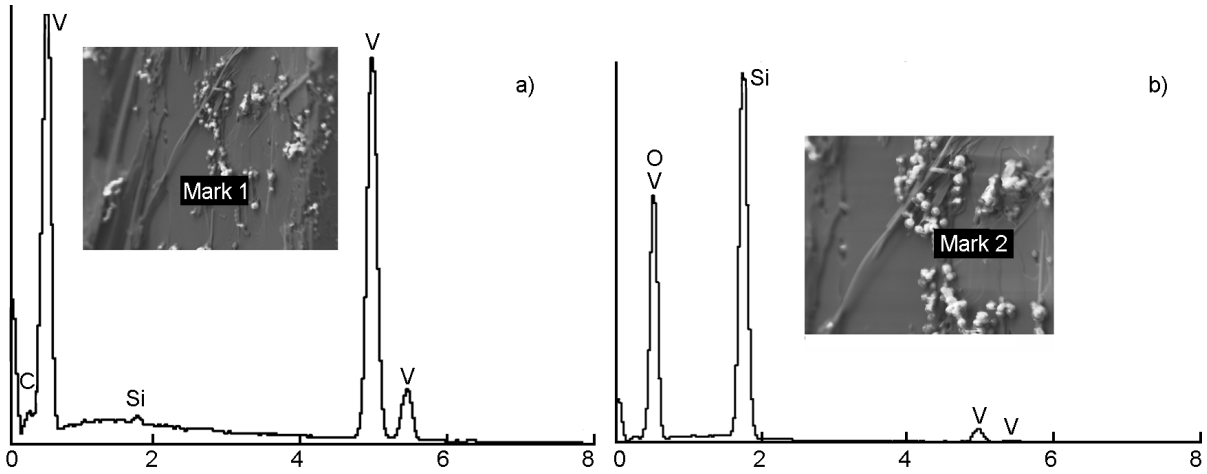

Fig. 4. X-ray microanalysis performed for V_2O_5 free pure surface sample (a) and for SiO_2 precipitates (b) as addition to V_2O_5 compound. The suitable test place signed as "mark 1" and "mark 2".

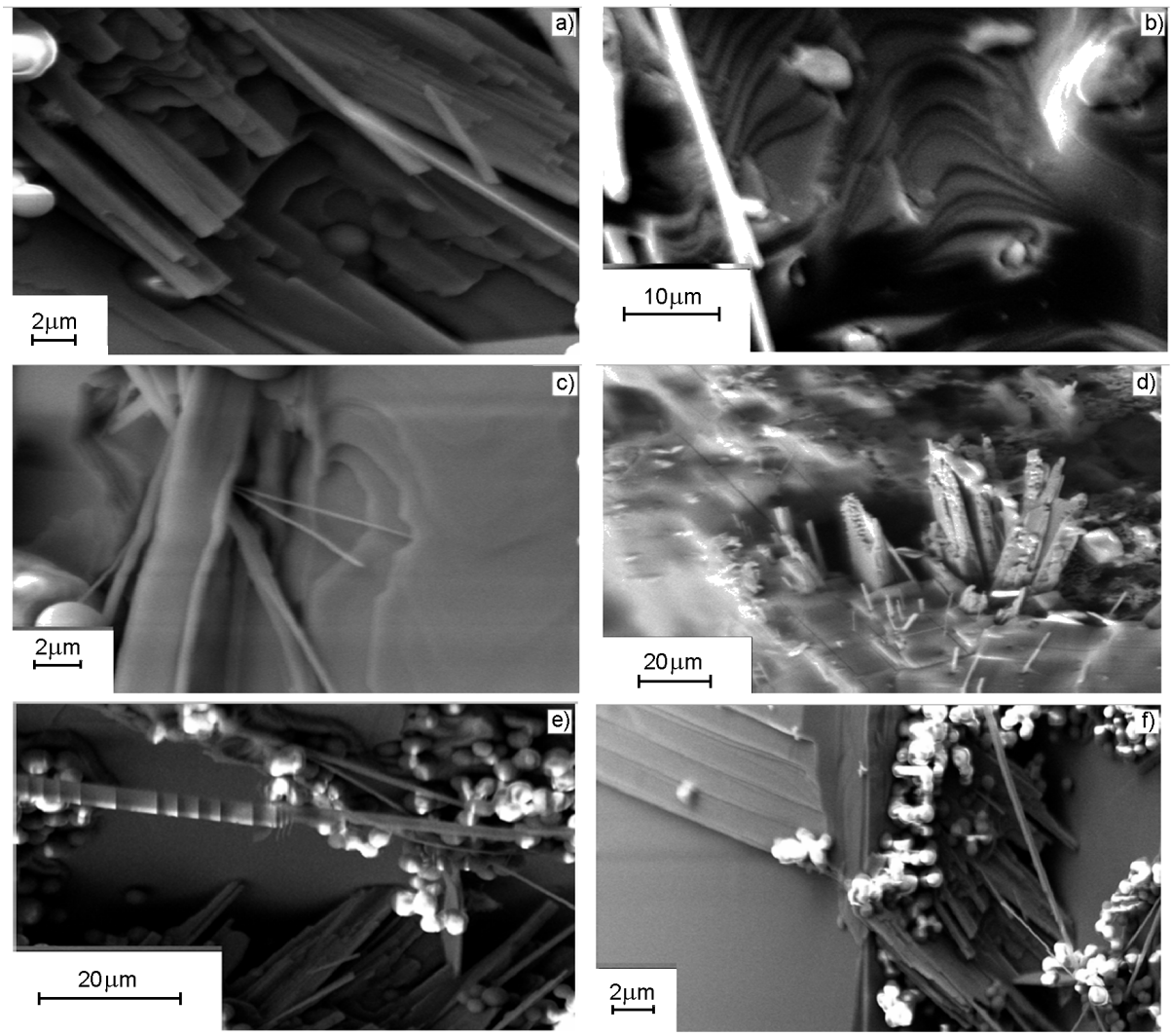

Fig. 5. SEM-images of the typical observed V_2O_5 crystalline structures: the synthesized lamellar microcrystals (a); terraced surface and elongated rod-shaped structures (b, c); needle-like and elongated formations (d); rod divided by sections (e) and stairs-like structures (f).

the [001] and [110] directions. Obtained data testify to dependence XRD-parameters on preliminary thermal treatment of starting materials. These differences most likely caused by vacancy defects of structure in oxygen sublattice.

The SEM-data (Fig. 3) for synthesized V_2O_5 crystal shows the real layer-like structure and testify about equilibrium growth process. Minimal visible (by microscope dimension) structure elements (Fig. 3) are about 100 nm. The data of element X-ray microanalysis are shown on Fig. 4. In crystals free for nanocrystalline SiO_2 (surface is free for SiO_2 aggregates of spherical-like form, as shown in the Fig. 4a) the basic elements of vanadium oxide samples – V and O are registered. The spherical-like formation (diameter is above 2–4 μm) is the SiO_2 phase (Fig. 4b).

Fig. 5(a–f) shown the typical observed micro- and nanostructures in samples. It is significant, that in undoped V_2O_5 samples the crystalline micro- and nanostructures are practically not observed. In the composite of V_2O_5/SiO_2 the SiO_2 presence together with layer nature of V_2O_5 structure caused the formation of observed crystalline nano- and micro-structures (Fig. 5).

Our synthesized nano- and micro-size crystalline structures (0.1÷0.5 μm minimal and 20÷150 μm maximal dimensions) are similar to the described data (see e.g. [2–5, 13–15], it these works synthesis was realized by different method). In this work formation of rod-shaped crystals, whiskers, and also lamellar crystals and planar ordered textures consisting of oriented rodious vanadium pentoxides was revealed. The terraced surface, divided rod by section, and stairs-like structures were occasionally observed (Fig. 5). The planar structures with a developed surface probably parallel to the cleavage plane were formed, and in the ensembles were grouped.

Evidently, the layering structure of vanadium pentoxide with controlled spacing between V–O layers is performed a leading role in formation of nanostructures. The introduction of SiO_2 nanopowder (as stimulant/template) causes the additional conditions for nanostructured V_2O_5 formation. The microcrystals deposition growing is realized in region of the micropores and also on the surface of the SiO_2 particles (Fig. 6) and on the exposed surfaces of the crystalline of V_2O_5 as on supporting materials.

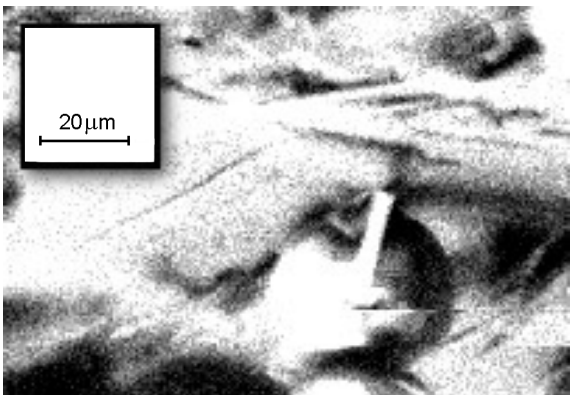

Fig. 6. Single nanorod deposited on surface of the particle SiO_2.

4. Conclusions

The formation of nano- and micro-structures of V_2O_5 was revealed under the complex conditions and, in particular, in intersurface positions with high flexion radius (curvature factor) as considered e. g. in works [16–18] for the growth of nanowires and other nanoformations.

In this work the proposed procedure is provided the possibility of the obtaining nano- and micro- size crystalline structures of V_2O_5 with different morphology. The changes of physicochemical conditions of synthesis caused the morphology and dimensions changes of the micro- and nano- structures of V_2O_5. The preliminary thermal treatment of starting material and special additions (nanopowder SiO_2) radically influenced on the formation of nano- and microcrystalline structures of V_2O_5.

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Одержання та спостереження нано- і мікро-розмірних кристалічних структур V_2O_5

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Розглянуто простий спосіб отримання мікро- та нанокристалічних структур на основі V_2O_5 у замкнутому об'ємі, близький до методу Бріджмена. За допомогою растрового електронного мікроскопа та Х-променевого дифракційного методу досліджено морфологічні особливості отриманих кристалічних структур. Коротко описано деякі структури V_2O_5, що спостерігалися, з врахуванням фізико-хімічних умов синтезу.