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Placing of hydrogen in titanium oxyhydride

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Received September 13, 2021
Revised September 13, 2021
Accepted September 26, 2021

Possible models of the arrangement of hydrogen atoms at the sites of the cubic lattice of titanium oxyhydride TiO_yH_p with vacancies in the metallic and nonmetallic sublattices are considered. It was found that titanium oxyhydride retains the $B1$ type crystal lattice of the initial cubic titanium monoxide TiO_y and contains structural vacancies in the metal and oxygen sublattices. Comparison of the found analytical expressions for the intensity of diffraction reflections with experimental X-ray and neutron diffraction data showed that interstitial H atoms in oxyhydrides occupy vacant octahedral positions $4(b)$ of the oxygen sublattice. No displacement of H atoms in tetrahedral positions $8(c)$ is observed. A disorder-order phase transition channel associated with the formation of an ordered monoclinic titanium oxyhydride of the Ti_5O_5 type was found. The distribution functions of Ti, O, and H atoms in the partially ordered monoclinic oxyhydride $Ti_{5.33}O_{5.12}H_{0.74}$ ($Ti_{0.89}O_{0.85}H_{0.12}$) with a Ti_5O_5-type structure are calculated for the first time, and the concentrations of these atoms at the positions of its lattice were found.

Keywords: Titanium monoxide, Hydrogen, Nonstoichiometry, Vacancies, Octahedral and tetrahedral positions, Distribution function.

DOI: 10.21883/PSS.2022.01.52485.202

1. Introduction

Non-stoichiometric cubic titanium monoxide $TiO_y \equiv Ti_xO_z$ ($Ti_x\blacksquare_{1-x}O_z\square_{1-z}$, where $y = z/x$, $\square$ and $\blacksquare$ are structural vacancies of the nonmetallic (oxygen) and metallic (titanium) sublattices) with a structure of the $B1$ type pertains to the group of strongly non-stoichiometric insertion compounds MX_y (M = Ti, Zr, Hf, V, Nb, Ta $X = C, N, O$) [1] and has a wide homogeneity region from $TiO_{0.80}$ to $TiO_{1.25}$. Atoms and structural vacancies in the unordered state are randomly distributed across the nodes of the corresponding sublattices. Cubic titanium monoxide with double deficiency and its oxyhydrides are the promising materials for hydrogen equipment, photocatalysis, water cleaning from impurities, particularly in the nanocrystalline state [2].

Non-stoichiometric compounds MX_y ($X = C, N, O$) with a structure of the $B1$ type may absorb hydrogen from the gaseous phase and form triple hydride phases MX_yH_p. As a rule, hydrogen atoms are located in vacant octahedral sites $4(b)$ of a nonmetallic sublattice. For instance, hydrogen atoms in cubic titanium and zirconium carbides occupy vacant nodes of a carbon sublattice, i.e. octahedral interstitial sites of a metal sublattice [3–7]. The neutron diffraction experiments [5,8] have showed that hydrogenation facilitates the ordering of carbon vacancies in some titanium carbides.

Neutron diffraction analysis of niobium carbohydrides [9,10] has found that H atoms in vacant octahedral sites are somewhat shifted from the center towards $[100]_{B1}$. The shift of H atoms in relation to the vacancy center is conditioned by a large vacancy volume, on the one hand, and a small hydrogen atom volume, on the other hand.

Thanks to the small size, H atoms in addition to vacant octahedral sites of a nonmetallic sublattice of carbides may occupy tetrahedral interstitial sites. Possible location of hydrogen atoms in tetrahedral interstitial sites follows from the data [11], according to which the relative hydrogen content, p, in some cubic titanium and niobium carbohydrides MC_yH_p ($TiC_{0.64}H_{0.38}$, $NbC_{0.77}H_{0.32}$–$NbC_{1.00}H_{0.25}$) may exceed the concentration of structural vacancies $(1-y)$ in a carbon sublattice.

Until late, the literature gave no data about the position of H atoms in cubic titanium oxyhydrides TiO_yH_p. It is usually supposed that hydrogen in oxyhydrides TiO_yH_p occupies vacant nodes $4(b)$ of an oxygen sublattice [12]. However, hydrogen atom sizes are such that it cannot invade both into octahedral and tetrahedral interstitial sites of a face-centered cubic (FCC) metal lattice. Therefore, it cannot be ruled out that at least a portion of hydrogen atoms can find place in tetrahedral interstitial sites of a FCC titanium lattice. In fact, all H atoms in cubic titanium hydride TiH_y with the hydrogen content of $y \leq 1.8$ and structure of $C1$ type (CaF_2) are located in tetrahedral sites $8(c)$ [13]. Thus, it is

not still clear in which sites of the crystalline structure of titanium oxyhydride the H atoms are located.

In this respect, the goal of this paper is modelling of the structure of cubic titanium oxyhydrides TiO_yH_p and determination of the position of H atoms in them by diffraction methods.

2. Results and discussion

The model of the structure of cubic (spatial group $Fm\bar{3}m$) titanium oxyhydride TiO_yH_p ($Ti_xO_zH_{px}$) with the position of items $4(a)$, $4(b)$ and $8(c)$ is shown in Fig. 1. Taking into account the possible hydrogen intrusion into octa- and tetra-interstitial sites of a cubic lattice, two variants of the model location of H atoms can be suggested for cubic titanium monoxide Ti_xO_z. In the first model that corresponds to a cubic structure of the $B1$ type, hydrogen may occupy only vacant sites $4(b)$ of an oxygen sublattice. In the second model, hydrogen may occupy both vacant sites $4(b)$ of an oxygen sublattice and a portion of tetra-interstitial sites, i.e. sites $8(c)$. This model corresponds to a cubic (spatial group $Fm\bar{3}m$) structure of the $D0_3$ type. In this case the formula of titanium oxyhydride, taking into account its structure, should be written as $TiO_yH_p \equiv Ti_xO_zH_{px} \equiv Ti_xO_zH^{4(b)}_{(p-q)x}H^{8(c)}_{qx} \equiv Ti_x\blacksquare_{1-x}O_zH^{4(b)}_{(p-q)x}\square_{1-z-(p-q)x}H^{8(c)}_{qx}$.

Let us discuss the crystallographic sites where hydrogen atoms can be located in titanium oxyhydrides and changes that may be observed in X-ray images and neutron-diffraction patterns for titanium oxyhydrides in case of location of hydrogen atoms only in sites $4(b)$ or in sites $4(b)$ and $8(c)$. For this, let us find the structure amplitudes F and structural factors F^2 of titanium monoxide $Ti_xO_z \equiv TiO_y$ $(y = z/x)$ with structure $B1$, titanium oxyhydride $Ti_xO_zH_{px} \equiv TiO_yH_p$ with structure $B1$ and oxyhydride $Ti_xO_zH_{px} \equiv Ti_xO_zH^{4(b)}_{(p-q)x}H^{8(c)}_{qx}$ with structure $D0_3$. Structure amplitude

$$F_{hkl} = \sum_j f_j \exp[-i2\pi(x_j h + y_j k + z_j l)]$$

(f_j is the atomic scattering factor; x_j, y_j, z_j are the coordinates of j-th atom) defines the intensity of diffraction reflections. Structure amplitude in the general case is a complex quantity, that's why the analysis of diffraction reflection intensities uses a structural factor F^2, equal to a squared modulus of structure amplitude (or product of structure amplitude by complex conjugate quantity F^*_{hkl}), i.e.

$$F^2_{hkl} = |F_{hkl}|^2 = F_{hkl}F^*_{hkl}. \quad (1)$$

Sites $4(a)$ in a cubic (spatial group $Fm\bar{3}m$) lattice with structure $B1$ have the coordinates (0 0 0), (1/2 1/2 0), (1/2 0 1/2), (0 1/2 1/2), while sites $4(b)$ have the coordinates (1/2 1/2 1/2), (0 0 1/2), (0 1/2 0) and (1/2 0 0). Taking into account the coordinates of sites $4(a)$ and $4(b)$,

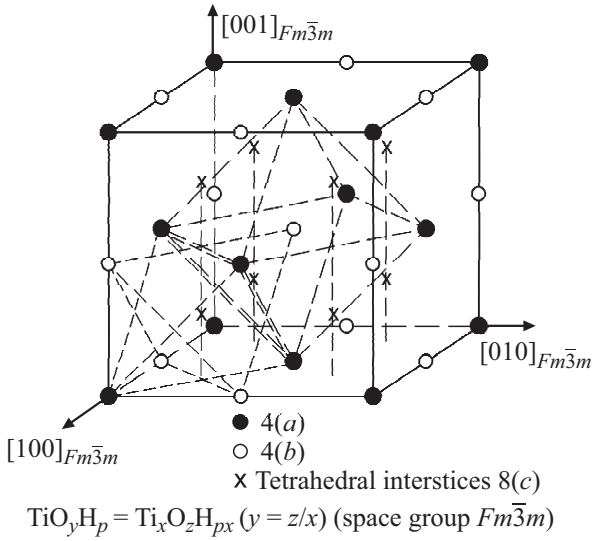

Figure 1. Model of structure of cubic (spatial group $Fm\bar{3}m$) titanium oxyhydride TiO_yH_p ($Ti_xO_zH_{px}$): (•) sites $4(a)$ — nodes of a metallic sublattice statistically occupied by Ti atoms; (○) sites $4(b)$ — nodes of a nonmetallic sublattice statistically occupied by O atoms; (×) sites $8(c)$ — centers of tetrahedral interstitial sites. Tetrahedral interstitial sites, formed by four nodes of a metallic sublattice (or four nodes of an oxygen sublattice), are showed by a short dashed line. While hydrogen atoms in oxyhydride TiO_yH_p ($Ti_xO_zH_{px}$) are located only in vacant sites $4(b)$ of an oxygen sublattice, the structure of the $B1$ type is retained. If a portion of H atoms in oxyhydride TiO_yH_p occupies vacant sites $4(b)$ of an oxygen sublattice, while the other H atoms are statistically located in tetrahedral sites $8(c)$, then oxyhydride structure type is $D0_3$.

with probabilities x and z statistically occupied by atoms of titanium Ti and oxygen O, respectively, structure amplitude F of cubic (spatial group $Fm\bar{3}m$) of titanium monoxide $Ti_xO_z \equiv TiO_y$ $(y = z/x)$ with structure $B1$ is equal to

$$F = x f_{Ti}\{1 + \exp[-i\pi(h+k)] + \exp[-i\pi(h+l)] + \exp[-i\pi(k+l)]\} + z f_O\{\exp[-i\pi(h+k+l)] + \exp(-i\pi h) + \exp(-i\pi k) + \exp(-i\pi l)]\}, \quad (2)$$

where f_{Ti} and f_O are the factors of radiation scattering by Ti and O atoms, respectively. In compliance with (1, 2), the structural factor F^2 for titanium monoxide Ti_xO_z with structure $B1$ is as follows

$$F^2_{B1}(hkl) = \{x f_{Ti}[1 + \cos\pi(h+k) + \cos\pi(h+l) + \cos\pi(k+l)] + z f_O[\cos\pi(h+k+l) + \cos\pi h + \cos\pi k + \cos\pi l]\}^2. \quad (3)$$

Sites $4(a)$ in titanium oxyhydride $Ti_xO_zH_{px}$ with structure $B1$ are statistically, with probability x, occupied by Ti atoms, while sites $4(b)$ are statistically, with probabilities z and px, occupied by O and H atoms,

respectively. Taking this into account, structure amplitude F of cubic (spatial group $Fm\bar{3}m$) titanium oxyhydride $\mathrm{Ti}_x\mathrm{O}_z\mathrm{H}_{px} \equiv \mathrm{TiO}_y\mathrm{H}_p$ with structure B1 is as follows

$$F = x f_{\mathrm{Ti}}\{1 + \exp[-i\pi(h+k)] + \exp[-i\pi(h+l)] + \exp[-i\pi(k+l)]\} + (z f_{\mathrm{O}} + px f_{\mathrm{H}})\{\exp[-i\pi(h+k+l)] + \exp(-i\pi h) + \exp(-i\pi k) + \exp(-i\pi l)]\}, \quad (4)$$

where f_{H} is the factor of radiation scattering by atoms of hydrogen H. The structural factor F^2 is equal to

$$F^2_{B1}(hkl) = \{x f_{\mathrm{Ti}}[1 + \cos\pi(h+k) + \cos\pi(h+l) + \cos\pi(k+l)] + (z f_{\mathrm{O}} + px f_{\mathrm{H}})[\cos\pi(h+k+l) + \cos\pi h + \cos\pi k + \cos\pi l]\}^2. \quad (5)$$

While hydrogen atoms in oxyhydride $\mathrm{Ti}_x\mathrm{O}_z\mathrm{H}_{px}$ can be located both in unfilled nodes of an oxygen sublattice (sites $4(b)$) and in tetra-interstitial sites (sites $8(c)$), titanium oxyhydride has a cubic (spatial group $Fm\bar{3}m$) structure of the $D0_3$ type and its formula can be written as $\mathrm{Ti}_x\mathrm{O}_z\mathrm{H}_{px} \equiv \mathrm{Ti}_x\mathrm{O}_z\mathrm{H}^{4(b)}_{(p-q)x}\mathrm{H}^{8(c)}_{qx}$. Sites $4(a)$ in such titanium oxyhydride are statistically, with probability x, occupied by Ti atoms, sites $4(b)$ are statistically, with probabilities z and $(p-q)x$, occupied by atoms of oxygen O and hydrogen H, respectively, and sites $8(c)$ are statistically, with probability $qx/2$, are occupied by H atoms. Sites $8(c)$ of a cubic (spatial group $Fm\bar{3}m$) lattice have the coordinates: (1/4 1/4 1/4), (3/4 3/4 1/4), (3/4 1/4 3/4), (1/4 3/4 3/4), (3/4 3/4 3/4), (1/4 1/4 3/4), (1/4 3/4 1/4) and (3/4 1/4 1/4). Taking into account the coordinates of sites $4(a)$, $4(b)$ and $8(c)$ and the probabilities of their filling with Ti, O and H atoms, the structure amplitude F for unordered cubic (spatial group $Fm\bar{3}m$) oxyhydride $\mathrm{Ti}_x\mathrm{O}_z\mathrm{H}^{4(b)}_{(p-q)x}\mathrm{H}^{8(c)}_{qx}$ with structure $D0_3$ is as follows

$$F = x\big[f_{\mathrm{Ti}}\{1 + \exp[-i\pi(h+k)] + \exp[-i\pi(h+l)] + \exp[-i\pi(k+l)]\} + \big(y f_{\mathrm{O}} + (p-q) f_{\mathrm{H}}\big) \times \{\exp[-i\pi(h+k+l)] + \exp(-i\pi h) + \exp(-i\pi k) + \exp(-i\pi l)\big]\} + (q f_{\mathrm{H}}/2)\{\exp[-i\pi(h+k+l)/2] + \exp[-i\pi(3h+3k+l)/2] + \exp[-i\pi(3h+k+3l)/2] + \exp[-i\pi(h+3k+3l)/2] + \exp[-i\pi(3h+3k+3l)/2] + \exp[-i\pi(h+k+3l)/2] + \exp[-i\pi(h+3k+l)/2] + \exp[-i\pi(3h+k+l)/2]\}. \quad (6)$$

In compliance with (6), the structural factor F^2 for unordered cubic (spatial group $Fm\bar{3}m$) titanium oxyhydride $\mathrm{Ti}_x\mathrm{O}_z\mathrm{H}^{4(b)}_{(p-q)x}\mathrm{H}^{8(c)}_{qx}$ with a structure of the $D0_3$ type is equal to

$$F^2_{DO_3}(hkl) = x^2\Big\{f_{\mathrm{Ti}}[1 + \cos\pi(h+k) + \cos\pi(h+l) + \cos\pi(k+l)] + [y f_{\mathrm{O}} + (p-q) f_{\mathrm{H}}][\cos\pi(h+k+l) + \cos\pi h + \cos\pi k + \cos\pi l] + \frac{q}{2} f_{\mathrm{H}}\Big[\cos\frac{\pi}{2}(h+k+l) + \cos\frac{\pi}{2}(3h+3k+l) + \cos\frac{\pi}{2}(3h+k+3l) + \cos\frac{\pi}{2}(h+3k+3l) + \cos\frac{\pi}{2}(3h+3k+3l) + \cos\frac{\pi}{2}(h+k+3l) + \cos\frac{\pi}{2}(h+3k+l) + \cos\frac{\pi}{2}(3h+k+l)\Big]\Big\}^2 + x^2\Big\{\frac{q}{2} f_{\mathrm{H}}\Big[\sin\frac{\pi}{2}(h+k+l) + \sin\frac{\pi}{2}(3h+3k+l) + \sin\frac{\pi}{2}(3h+k+3l) + \sin\frac{\pi}{2}(h+3k+3l) + \sin\frac{\pi}{2}(3h+3k+3l) + \sin\frac{\pi}{2}(h+k+3l) + \sin\frac{\pi}{2}(h+3k+3l) + \sin\frac{\pi}{2}(3h+k+l)\Big]\Big\}^2. \quad (7)$$

It follows from formulas (5) and (7) that filling of sites $8(c)$ with H atoms does not lead to the formation of new diffraction reflections, but only insignificantly changes the value of the structural factors (Table 1). Therefore, unordered cubic oxyhydrides $\mathrm{Ti}_x\mathrm{O}_z\mathrm{H}_{px}$ with structures $B1$ and $D0_3$ have an identical set of diffraction reflections. Since the factor of X-ray scattering by H atoms is very low as compared to the factors of scattering by Ti and O atoms, hydrogen intrusion slightly affects the intensity of X-ray reflections. However, X-ray diffraction allows for revealing the ordering of Ti and O atoms in titanium monoxide or oxyhydride.

The situation is completely different in the case of neutron diffraction measurements. Amplitudes of coherent scattering of neutrons by Ti, ^{16}O and ^{1}H nuclei are equal to $-3.438 \cdot 10^{-15}$, $5.803 \cdot 10^{-15}$ and $-3.741 \cdot 10^{-15}$ m, respectively [14,15]. Neutron scattering amplitudes f_{Ti} and f_{O} are opposite in sign, therefore, the structural factors of even reflections even in titanium monoxide are very low as compared to the structural factors of odd reflections. Thanks to the negative amplitude of neutron scattering by ^{1}H nuclei, hydrogen intrusion into titanium monoxide causes even a greater relative decrease of the structural factors F^2 of even reflections (200), (220), (222), (400), (420) and (422) as compared to factors F^2 of odd reflections (111), (311), (331) and (511). In case of hydrogen intrusion only in vacant sites $4(b)$, i.e. in

Table 1. Structural factors F^2 for cubic (spatial group $Fm\bar{3}m$) titanium monoxide $Ti_xO_z \equiv TiO_y$ (structure $B1$) and titanium oxyhydrides $Ti_xO_zH_{px} \equiv TiO_yH_p$ (structures $D0_3$ and $B1$) (P is the multiplicity factor)

(hkl)	P	F^2		
		$Ti_xO_z \equiv TiO_y$ $(y = z/x)$, $B1$	$Ti_xO_zH_{px} \equiv Ti_xO_zH^{4(b)}_{(p-q)x}H^{8(c)}_{qx}$, $D0_3$	$Ti_xO_zH_{px} \equiv TiO_yH_p$ $(y = z/x)$, $B1$
111	8	$16x^2(f_{Ti}-yf_O)^2$	$16x^2\{f_{Ti}-[yf_O+(p-q)f_H]\}^2$	$16x^2[f_{Ti}-(yf_O+pf_H)]^2$
200	6	$16x^2(f_{Ti}+yf_O)^2$	$16x^2[f_{Ti}+yf_O+(p-2q)f_H]^2$	$16x^2(f_{Ti}+yf_O+pf_H)^2$
220	12	$16x^2(f_{Ti}+yf_O)^2$	$16x^2(f_{Ti}+yf_O+pf_H)^2$	$16x^2(f_{Ti}+yf_O+pf_H)^2$
311	24	$16x^2(f_{Ti}-yf_O)^2$	$16x^2\{f_{Ti}-[yf_O+(p-q)f_H]\}^2$	$16x^2[f_{Ti}-(yf_O+pf_H)]^2$
222	8	$16x^2(f_{Ti}+yf_O)^2$	$16x^2[f_{Ti}+yf_O+(p-2q)f_H]^2$	$16x^2(f_{Ti}+yf_O+pf_H)^2$
400	6	$16x^2(f_{Ti}+yf_O)^2$	$16x^2(f_{Ti}+yf_O+pf_H)^2$	$16x^2(f_{Ti}+yf_O+pf_H)^2$
331	24	$16x^2(f_{Ti}-yf_O)^2$	$16x^2f_{Ti}-[yf_O+(p-q)f_H]^2$	$16x^2[f_{Ti}-(yf_O+pf_H)]^2$
420	24	$16x^2(f_{Ti}+yf_O)^2$	$16x^2[f_{Ti}+yf_O+(p-2q)f_H]^2$	$16x^2(f_{Ti}+yf_O+pf_H)^2$
422	24	$16x^2(f_{Ti}+yf_O)^2$	$16x^2(f_{Ti}+yf_O+pf_H)^2$	$16x^2(f_{Ti}+yf_O+pf_H)^2$
333	8	$16x^2(f_{Ti}-yf_O)^2$	$16x^2\{f_{Ti}-[yf_O+(p-q)f_H)]\}^2$	$16x^2[f_{Ti}-(yf_O+pf_H)]^2$
511	24	$16x^2(f_{Ti}-yf_O)^2$	$16x^2\{f_{Ti}-[yf_O+(p-q)f_H)]\}^2$	$16x^2[f_{Ti}-(yf_O+pf_H)]^2$

oxyhydride TiO_yH_p ($Ti_xO_zH_{px}$), the structural factors F^2 (exclusive of angular intensity attenuation) for all even reflections are equal to $16x^2(f_{Ti}+yf_O+pf_H)^2$ (Table 1). If hydrogen is also located in sites $8(c)$ and oxyhydride $Ti_xO_xH^{4(b)}_{(p-q)x}H^{8(c)}_{qx}$ has a structure of the $D0_3$ type, then the structural factors $F^2 = 16x^2(f_{Ti}+yf_O+pf_H)^2$ for even reflections (hkl) with $(h+k+l) = 4n$ (where n is an integer number), are less than the structural factors $F^2 = 16x^2[f_{Ti}+yf_O+(p-2q)f_H]^2$ for the rest even reflections. That's why clarification of the structure by analyzing the ratio of intensities of neutron diffraction reflections makes it possible to determine the sites occupied by hydrogen in titanium oxyhydride.

To find out the sites occupied by hydrogen atoms in titanium oxyhydrides, we have obtained quenched samples of unordered titanium monoxide $TiO_{0.72}$ ($Ti_{0.95}\blacksquare_{0.05}O_{0.69}\square_{0.31}$) and $TiO_{0.96}$ ($Ti_{0.89}\blacksquare_{0.11}O_{0.85}\square_{0.15}$) with structural vacancies both in the titanium sublattice and in the oxygen sublattice. The conditions of titanium monoxide synthesis in the unordered and ordered states were detailed earlier [16,17]. Both quenched samples contained only an unordered cubic (spatial group $Fm\bar{3}m$) phase of TiO_y with a structure of the $B1$ type, period a_{B1} of the crystalline lattice of unordered monoxides $TiO_{0.72}$ and $TiO_{0.96}$ is equal to 0.41934 and 0.41827 nm, respectively. The composition of the $TiO_{0.96}$ sample is close to the equiatomic monoxide $TiO_{1.00}$, where a monocline (spatial group $C2/m$) ordered phase Ti_5O_5 forms at a temperature below 1250–1300 K ($Ti_5\blacksquare O_5\square$) [18].

Hydrogenation of quenched unordered samples of cubic titanium monoxide TiO_y was performed in a Sieverts vacuum system in hydrogen H_2 at the atmospheric pressure and temperature of 973 K.

The crystalline structure of samples of titanium monoxide $TiO_y \equiv Ti_xO_z$ and hydrogenated samples of $TiO_yH_p \equiv Ti_xO_zH_{px}$ was studied in the Shimadzu XRD-7000 X-ray autodiffraction meter by the Bragg–Brentano method in Cu$K\alpha_{1,2}$-emission in the interval of angles 2θ from 10 to 157° with a step of $\Delta(2\theta) = 0.02°$ and exposure for 10 s at each point. Distribution of atoms of hydrogen H in the crystalline lattice of titanium oxyhydrides TiO_yH_p was studied by the neutron crystallography method in a high-resolution powder diffraction meter BT1 [19] at the Neutron Research Center of NIST (Gaithersburg, MD, USA). Neutron wavelength was equal to 0.15401 nm, neutron-diffraction patterns were recorded in the angle interval $5 \le 2\theta \le 162°$ with the step of $\Delta(2\theta) = 0.05°$.

Determination of samples' phase composition and parameters of phases' crystalline lattice, as well as final clarification of sample structure was performed using the X'Pert Plus software package [20]. The profile of diffraction reflections was modelled by the pseudo-Voigt function, the background was described by a Chebyshev polynomial of the 5-th order.

Hydrogenation of unordered titanium monoxide $TiO_{0.72}$ resulted in the formation of cubic (spatial group $Fm\bar{3}m$) oxyhydride $TiO_{0.72}H_{0.30}$ with the crystalline lattice spacing of 0.42076 nm (Fig. 2) [21]. Lattice spacing increase from 0.41934 to 0.42076 nm is due to the intrusion of a large amount of hydrogen into the crystalline lattice of monoxide TiO_y.

Clarification of the structure of single-phase oxyhydride $TiO_{0.72}H_{0.30}$ using the X'Pert Plus program [20] and with account of structural factors F^2 (see Table 1) yielded the following results. When describing the neutron-diffraction pattern (Fig. 2, *b*), Rietveld convergence factors in the model with structure $B1$ are equal to $R_{exp} = 0.067$, $R_p = 0.055$, $R_{wp} = 0.072$ and $R_I(R_{Bragg}) = 0.015$. The use of a model of the structure of $D0_3$ type with location of a quarter of all hydrogen atoms in tetrahedral sites (in this case, degree of filling of the tetrahedral sites $8(c)$ by H atoms is equal to 0.036) has caused deterioration of convergence: $R_{exp} = 0.069$, $R_p = 0.056$, $R_{wp} = 0.073$

and $R_{\mathrm{I}}(R_{\mathrm{Bragg}}) = 0.018$. An increase in the degree of filling of sites $8(c)$ by H atoms from 0.036 to 0.144, i.e. location of all hydrogen atoms in tetrahedral sites $8(c)$ has further deteriorated the convergence of the experimental and calculated diffraction patterns. Thus, clarification of the structure of oxyhydride $TiO_{0.72}H_{0.30}$ using X-ray and neutron diffraction data has showed that this oxyhydride has a cubic (spatial group $Fm\bar{3}m$) structure of the $B1$ type, where all hydrogen atoms are in sites $4(b)$. Taking into account the degrees of filling of sites $4(a)$ by Ti atoms and sites $4(b)$ by O and H atoms, the oxyhydride composition is $Ti_{0.96}O_{0.69}H_{0.29}$.

Hydrogenation of the $TiO_{0.96}$ sample has caused not only the formation of oxyhydride $TiO_{0.96}H_{0.14}$, but a second phase has appeared along with the cubic phase. Analysis of the diffraction data (Fig. 3) has showed

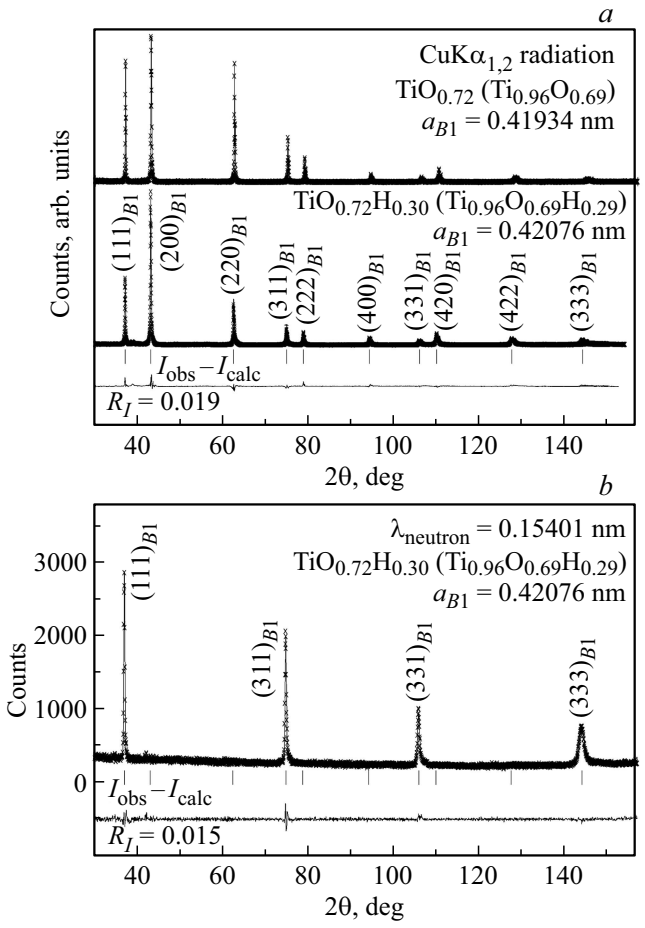

Figure 2. X-ray images (a) for the initial unordered cubic titanium monoxide $TiO_{0.72}$ ($Ti_{0.96}O_{0.69}$) and titanium oxyhydride $TiO_{0.72}H_{0.30}$ ($Ti_{0.96}O_{0.69}H_{0.29}$) and neutron-diffraction pattern (b) for titanium oxyhydride $TiO_{0.72}H_{0.30}$ ($Ti_{0.96}O_{0.69}H_{0.29}$) ($\times$ is the experiment, solid line is the calculation). The long dashes correspond to diffraction reflections of unordered cubic (spatial group $Fm\bar{3}m$) titanium oxyhydride $TiO_{0.72}H_{0.30}$ with structure $B1$. The lower part of Figures (a) and (b) shows the differences ($I_{\mathrm{obs}}-I_{\mathrm{calc}}$) between the experimental and calculated diffraction patterns for titanium oxyhydride $TiO_{0.72}H_{0.30}$.

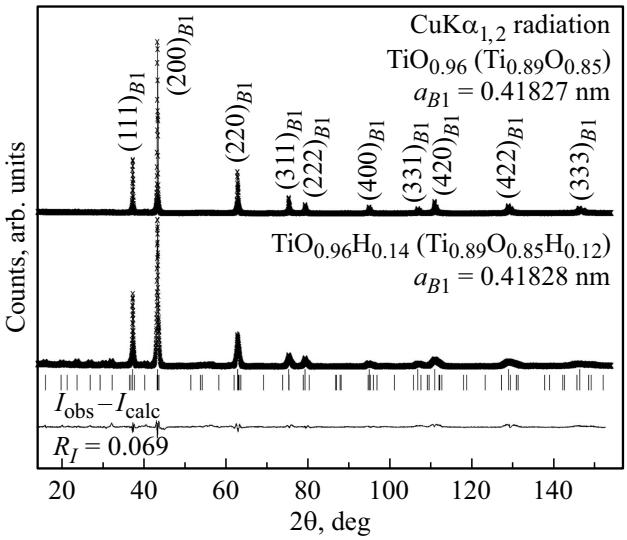

Figure 3. X-ray images for the initial unordered cubic titanium monoxide $TiO_{0.96}$ ($Ti_{0.89}O_{0.85}$) and titanium oxyhydride $TiO_{0.96}H_{0.14}$ ($Ti_{0.89}O_{0.85}H_{0.12}$) ($\times$ is the experiment, solid line is the calculation). The initial monoxide $TiO_{0.96}$ contains only an unordered cubic (spatial group $Fm\bar{3}m$) phase with structure $B1$. Titanium oxyhydride $TiO_{0.962}H_{0.14}$ is two-phase and contains $\sim 86 \pm 2$ wt.% of the unordered cubic (spatial group $Fm\bar{3}m$) phase with structure $B1$ and $\sim 14 \pm 2$ wt.% of the ordered monocline (spatial group $C2/m$) phase of the Ti_5O_5 type. The long and short dashes are the positions of the diffraction reflections of unordered cubic titanium oxyhydride $TiO_{0.96}H_{0.14}$ with structure $B1$ and ordered monocline phase $Ti_{5.33}\blacksquare_{0.67}O_{5.12}H_{0.74}\square_{0.14}$ of the Ti_5O_5 type, respectively. ($I_{\mathrm{obs}}-I_{\mathrm{calc}}$) is the difference between the experimental and calculated X-ray images for titanium oxyhydride $TiO_{0.96}H_{0.14}$.

that oxyhydride $TiO_{0.96}H_{0.14}$ contains an unordered cubic phase $Ti_{0.89}O_{0.85}H_{0.12}$ in the amount of $\sim 86 \pm 2$ wt.% and an ordered monocline (spatial group $C2/m$) phase of the Ti_5O_5 type in the amount of $\sim 14 \pm 2$ wt.%. The lattice spacing for the cubic oxyhydride phase is equal to $a_{B1} = 0.41828$ nm, i.e. it has insignificantly (within the measurement error) increased due to hydrogen intrusion into vacant sites of the oxygen sublattice. The formation of a monocline ordered phase of the Ti_5O_5 type was due to low-temperature annealing of a $TiO_{0.96}$ sample, since monoxide composition and hydrogenation temperature ~ 970 K correspond to the region of equilibrium existence of a superstructure of the Ti_5O_5 type.

When describing the X-ray image (Fig. 3) for oxyhydride $TiO_{0.96}H_{0.14}$, the best convergence of the experiment and the calculation has been attained in case of statistical placement of all hydrogen atoms in vacant octahedral sites of the oxygen sublattice: in case of an unordered cubic phase these are sites $4(b)$, and in the monocline phase these are sites $2(c)$.

The performed quantitative analysis of the structural X-ray data has showed that the second phase (ordered monocline oxyhydride of the Ti_5O_5 type) present in oxyhydride $TiO_{0.96}H_{0.14}$ has the composition $Ti_{5.33}\blacksquare_{0.67}O_{5.12}H_{0.74}\square_{0.14}$

Table 2. Monocline (spatial group $C2/m$) oxyhydride phase $Ti_{5.33}O_{5.12}H_{0.74}$ with a structure of the Ti_5O_5 type ($a_m = 0.58488$ nm, $b_m = 0.41473$ nm, $c_m = 0.94562$ nm, $\beta = 108.26°$), contained in two-phase oxyhydride $TiO_{0.96}H_{0.14}$ in the amount of $\sim 14 \pm 2$ wt.%

Atom	Site and multiplicity	Atomic coordinates in the ordered phase			Atomic coordinates in the basic structure $B1$			Values of distribution functions $n_{Ti}(x_I y_I, z_I)$, $n_O(x_I, y_I, z_I)$ and $n_H(x_I, y_I, z_I)$
		x/a_m	y/b_m	z/c_m	x_I	y_I	z_I	
Ti 1 (vacancy)	2(a)	0	0	0	0	0	0	$n_{1(Ti)} = x - \eta_{10}^{Ti}/6 - \eta_4^{Ti}/3 - \eta_1^{Ti}/3 \approx 0.328$
Ti 2	2(d)	1/2	1/2	1/2	1	1/2	1/2	$n_{2(Ti)} = x + \eta_{10}^{Ti}/6 - \eta_4^{Ti}/3 + \eta_1^{Ti}/3 \approx 1$
Ti 3	4(i)	0.1654	0	0.3425	0.5079	0	0.5196	$n_{3(Ti)} = x + \eta_{10}^{Ti}/6 + \eta_4^{Ti}/6 - \eta_1^{Ti}/6 \approx 1$
Ti 4	4(i)	0.3218	0	0.6652	0.9870	0	1.0086	$n_{4(Ti)} = x - \eta_{10}^{Ti}/6 + \eta_4^{Ti}/6 + \eta_1^{Ti}/6 \approx 1$
O 1 (vacancy)	2(c)	1/2	0	1/2	1	0	1/2	$n_{1(O)} = z - \eta_{10}^{O}/6 - \eta_4^{O}/3 - \eta_1^{O}/3 \approx 0.124$
O 2	2(b)	0	1/2	0	0	1/2	0	$n_{2(O)} = z + \eta_{10}^{O}/6 - \eta_4^{O}/3 + \eta_1^{O}/3 \approx 1$
O 3	4(i)	0.3364	0	0.1681	0.5045	0	0.0002	$n_{3(O)} = z + \eta_{10}^{O}/6 + \eta_4^{O}/6 - \eta_1^{O}/6 \approx 1$
O 4	4(i)	0.1668	0	0.8322	0.0010	0	0.4976	$n_{4(O)} = z - \eta_{10}^{O}/6 + \eta_4^{O}/6 + \eta_1^{O}/6 \approx 1$
H 1 (vacancy)	2(c)	1/2	0	1/2	1	0	1/2	$n_{1(H)} = px + \eta_{10}^{H}/6 + \eta_4^{H}/3 + \eta_1^{H}/3 \approx 0.744$
H 2	2(b)	0	1/2	0	0	1/2	0	$n_{2(H)} = px - \eta_{10}^{H}/6 + \eta_4^{H}/3 - \eta_1^{H}/3 \approx 0$
H 3	4(i)	0.3364	0	0.1681	0.5045	0	0.0002	$n_{3(H)} = px - \eta_{10}^{H}/6 - \eta_4^{H}/6 + \eta_1^{H}/6 \approx 0$
H 4	4(i)	0.1668	0	0.8322	0.0010	0	0.4976	$n_{4(H)} = px + \eta_{10}^{H}/6 - \eta_4^{H}/6 - \eta_1^{H}/6 \approx 0$

($Ti_{0.89}O_{0.85}H_{0.12}$) (Table 2). According to [17] and the performed analysis, ordered monocline oxyhydride of the Ti_5O_5 type forms along the phase transition channel, including one beam of the Lifshitz star $\{\mathbf{k}_{10}\}$ and two beams of non-Lifshitz stars $\{\mathbf{k}_4\}$ and $\{\mathbf{k}_1\}$ each (numbering of stars $\{\mathbf{k}_s\}$ of the wave vectors is given in compliance with [1,22]).

The performed calculation has showed that the functions of distribution of titanium, oxygen and hydrogen atoms in the observed monocline superstructure of the Ti_5O_5 type for oxyhydride $Ti_{0.89}O_{0.85}H_{0.12}$ with $x = 0.89$, $z = 0.85$ and $px = 0.12$ are as follows

$$n_{Ti}(x_I, y_I, z_I) = x - (\eta_{10}^{Ti}/6)\cos 2\pi z_I - (\eta_4^{Ti}/3)\cos[4\pi(x_I + z_I)/3] - (\eta_1^{Ti}/3)\cos[2\pi(2x_I - z_I)/3], \quad (8)$$

$$n_O(x_I, y_I, z_I) = z + (\eta_{10}^{O}/6)\cos 2\pi z_I - (\eta_4^{O}/3)\cos[4\pi(x_I + z_I)/3] + (\eta_1^{O}/3)\cos[2\pi(2x_I - z_I)/3], \quad (9)$$

$$n_H(x_I, y_I, z_I) = px - (\eta_{10}^{H}/6)\cos 2\pi z_I + (\eta_4^{H}/3)\cos[4\pi(x_I + z_I)/3] - (\eta_1^{H}/3)\cos[2\pi(2x_I - z_I)/3]. \quad (10)$$

In functions (8), (9) and (10) $n(x_I, y_I, z_I)$ — probability of location of the corresponding atom in node $\mathbf{r}$ of an ordering sublattice with the basic cubic coordinates x_I, y_I, z_I; η_s $(\eta_{10}, \eta_4, \eta_1)$ — long-range order parameters corresponding to stars $\{\mathbf{k}_{10}\}$, $\{\mathbf{k}_4\}$ and $\{\mathbf{k}_1\}$. [17] has showed that the parameters η_s, describing a specific sublattice, in a superstructure of the Ti_5O_5 type are equal, but each sublattice has its own value of η_s. Ratios $x_I = x_m + z_m$, $y_I = y_m$ and $z_I = -x_m + 2z_m$ are used for a transition from monocline coordinates to cubic ones. According to the calculation, in an approximation of equal long-range order parameters for titanium, oxygen and hydrogen sublattices $\eta_{10}^{Ti} = \eta_4^{Ti} = \eta_1^{Ti} \approx 0.674$, $\eta_{10}^{O} = \eta_4^{O} = \eta_1^{O} \approx 0.871$ and $\eta_{10}^{H} = \eta_4^{H} = \eta_1^{H} \approx 0.749$.

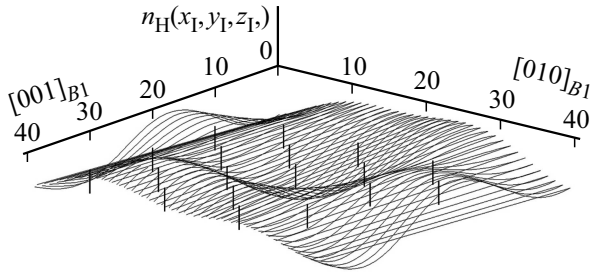

Figure 4. Distribution function $n_H(x_I, y_I, z_I)$ (10) of hydrogen atoms in the plane $(1\ -1\ 1)_{B1}$ of monocline (spatial group $C2/m$) titanium oxyhydride $Ti_{5.33}O_{5.12}H_{0.74}$. The position of hydrogen sublattice nodes, occupied by H atoms with probability ~ 0.74, is showed by vertical lines.

Figure 4, by way of example, shows the distribution function $n_H(x_I, y_I, z_I)$ (10) of hydrogen atoms in the plane $(1\ -1\ 1)$ of monocline (spatial group $C2/m$) titanium oxyhydride $Ti_{5.33}O_{5.12}H_{0.74}$ and the position of hydrogen sublattice nodes, occupied by H atoms with probability ~ 0.74.

3. Conclusion

The study of the structure of titanium oxyhydrides TiO_yH_p has showed that oxyhydrides retain a crystalline lattice of the $B1$ type for the initial cubic monoxides and contain structural vacancies in the metallic and oxygen sublattices. Interstitial hydrogen atoms in

cubic (spatial group $Fm\bar{3}m$) oxyhydrides occupy vacant octahedral sites $4(b)$ of the oxygen sublattice; hydrogen location in tetrahedral sites $8(c)$ is not observed. Upon formation of a monocline (spatial group $C2/m$) oxyhydride ordered phase of the Ti_5O_5 type, H atoms are located only in vacant octahedral sites $2(c)$ of the oxygen sublattice, i.e. surrounded by six titanium sublattice nodes.

Acknowledgements

The authors would like to thank A.V. Skripov (M.N. Mikheev Institute of Metal Physics of the Ural Branch of the Russian Academy of Sciences) for hydrogenation of titanium monoxides, H. Wu and T.J. Udovic (NIST Center for Neutron Research, Gaithersburg, USA) for assistance in neutron diffraction measurements.

Funding

The work has been carried out under state assignment No. 0397-2019-0001 at the Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences.

Conflict of interest

The authors declare that they have no conflict of interest.

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