

PHYSICAL METHODS
OF INVESTIGATION

Neutron Diffraction Study of Titanium Carbide TiC_x Prepared from Hydrogen-Containing Titanium Powder

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Abstract—We show that self-propagating high-temperature synthesis can serve to prepare not only stoichiometric or near-stoichiometric hydrogen-containing titanium carbide TiC_x from powdery titanium containing minor hydrogen. The hydrogen percentage in the crystal lattice increases linearly as the TiC_x composition progressively deviates from the 1 : 1 stoichiometry. A small amount of hydrogen atoms (within 0.38 wt %) in the crystal lattice of nonstoichiometric FCC titanium carbide TiC_x appreciably increases the unit cell parameter without having any effect on the concentration dependence trend. This result makes it possible to attest titanium carbide for hydrogen content from the unit cell versus concentration curve.

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Face-centered cubic (FCC) titanium carbide of variable composition, TiC_x ($x = 0.33\text{--}1.00$), has found extensive use in advanced engineering and industries [1] and in medicine [2] due to its high melting point, high hardness, and corrosion resistance. The precursors used for preparing TiC_x are carbon and titanium powders. Some types of titanium powders frequently contain minor hydrogen. If so, the final titanium carbide product can also contain minor hydrogen. This is disregarded by engineers. Meanwhile, this minor hydrogen can have an appreciate effect on the structure [3] and properties of titanium carbide [4].

Here we report on a neutron diffraction study of hydrogen content in titanium carbide TiC_x produced from powdery titanium containing minor hydrogen.

EXPERIMENTAL

The initial reagents used were fine carbon powder (high-purity grade) and titanium powder (PTM grade; 98.92 wt %; 0.38 wt % hydrogen; and 0.70 wt % the total of N_2 , C, Fe + Ni, Si, Ca, and Cl according to the certificate). The average titanium powder size was $\bar{r} = 40 \mu\text{m}$. Samples were prepared by self-propagating high-temperature synthesis in a constant-pressure bomb [5]. The titanium and carbon powders in required amounts and proportions were measured on an analytical balance and carefully pounded with an agate mortar and a pestle, and then compacted into a cylindrical briquette under $3 \times 10^6 \text{ N/m}^2$. Sample weights after the synthesis were monitored by comparing to the overall batch weight before the synthesis. All as-synthesized samples were homogenized by annealing in a CNOL furnace at 1475 K for 24 h. Hydrogen volatilization at the homogenization temperature was

inhibited by using evacuated and sealed off ampoules. As-annealed samples were quenched in water to fix an unordered FCC phase in the samples in order to preclude possible phase transformations upon slow lowering [3].

Carbon and hydrogen in samples were determined by chemical analysis at the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences. Hydrogen determination involved burning a sample in flowing oxygen, followed by weighing the water formed as a result of burning. Oxygen determination involved burning a weighed sample taking into account the absorption of nascent CO_2 . The results of chemical analysis and the elemental compositions of test samples are listed in Table 1. The chemical analysis accuracy was $\pm 0.3\%$.

Table 1. Chemical compositions (in weight percent) of test samples

Chemical formula	Ti	C	H ₂
$\text{TiC}_{1.00}$	79.89	20.12	N.D.
$\text{TiC}_{0.97}$	80.12	19.50	N.D.
$\text{TiC}_{0.80}\text{H}_{0.08}$	82.42	16.50	0.14
$\text{TiC}_{0.75}\text{H}_{0.10}$	83.27	15.65	0.17
$\text{TiC}_{0.70}\text{H}_{0.14}$	84.17	14.75	0.24
$\text{TiC}_{0.60}\text{H}_{0.17}$	86.04	12.88	0.30
$\text{TiC}_{0.55}\text{H}_{0.19}$	86.94	11.98	0.34
$\text{TiC}_{0.50}\text{H}_{0.21}$	87.91	11.01	0.38
$\text{TiC}_{0.47}\text{H}_{0.21}$	88.50	10.42	0.38

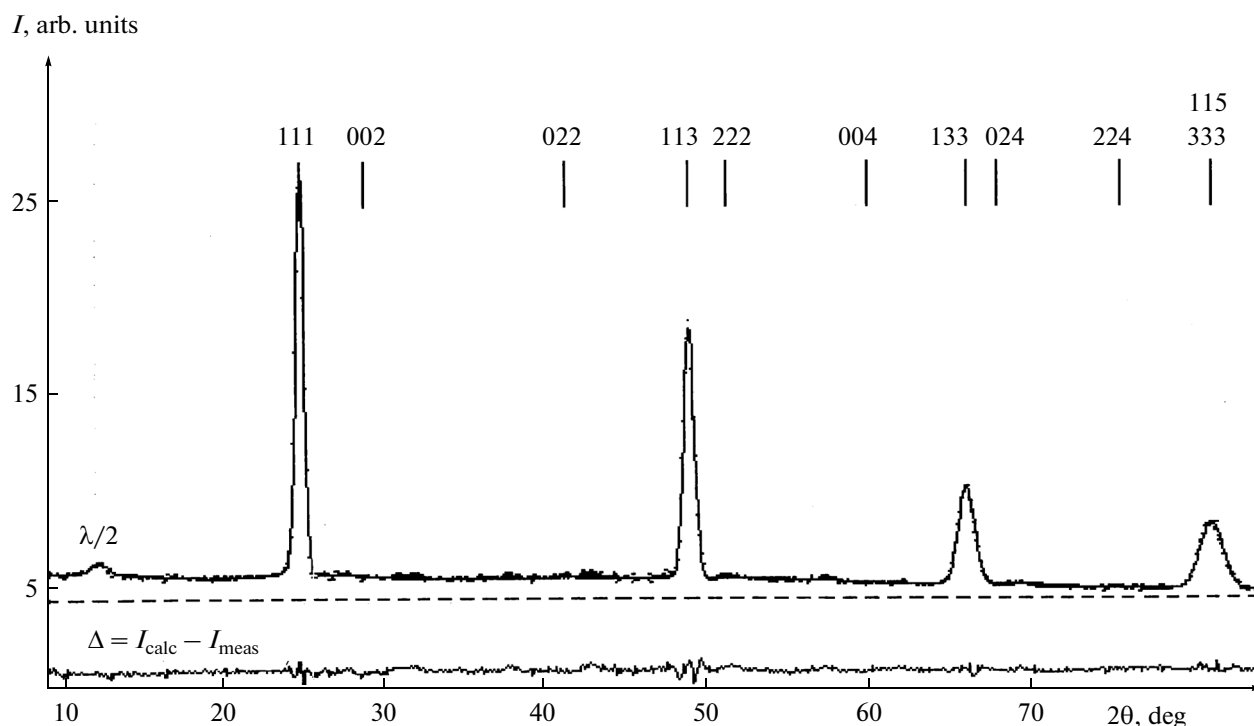


Fig. 1. Neutron diffraction pattern of titanium carbide $\text{TiC}_{0.50}$ containing minor hydrogen ($\text{TiC}_{0.50}\text{H}_{0.21}$): solid line shows the calculated curve; dots are datapoints; Δ is the difference curve. over diffraction peaks The Miller indices of reflecting planes of the crystal lattice in the frame of space group $Fm\bar{3}m$ are indicated above diffraction peaks. The horizontal dashed line indicates the background.

Neutron diffraction patterns were recorded on a DN-500 neutron diffractometer mounted on the thermal column of a VVR-SM nuclear reactor at the Institute of Nuclear Physics, Uzbekistan Academy of Sciences ($\lambda = 0.1085$ nm). Neutron diffraction is a tool to reliably determine the content and arrangement of hydrogen and light atoms in the crystal lattice because of neutron coherent scattering amplitudes b from metal and metalloids atoms having commensurate absolute values ($b_{\text{Ti}} = -0.34 \times 10^{-5}$ nm, $b_{\text{C}} = 0.665 \times 10^{-5}$ nm, and $b_{\text{H}} = -0.3745 \times 10^{-5}$ nm [6]). The neutron diffraction patterns were processed by the full-profile Rietveld analysis using DBW 3.2 software [7]. X-ray diffraction was used, for its high resolution, to evaluate the phase constitution and homogeneity of samples. X-ray diffraction patterns were recorded on a DRON-3M X-ray diffractometer ($\text{CuK}\alpha$, $\lambda_{\text{avg}} = 0.5418$ nm) in the range $2\theta = 10^\circ - 110^\circ$ with a detector rotation speed of 1 deg/min. In order to determine unit cell parameters, a narrow diffraction peak range was recorded with a detector rotation speed of 1/4 deg/min at $2\theta > 101^\circ$.

RESULTS AND DISCUSSION

X-ray powder diffraction shows that the samples prepared were single phases and homogeneous and had an FCC lattice (space group $Fm\bar{3}m$). Neutron dif-

fraction measurements support the results obtained by X-ray powder diffraction. Carbon and hydrogen contents of the samples were also derived by minimizing the divergence factors of crystal structure determination by the full-profile analysis of a neutron diffraction pattern. There is consistency between the results of chemical and neutron diffraction analyses. Table 1 makes it clear that a titanium powder containing minor hydrogen can serve to prepare not only stoichiometric or near-stoichiometric hydrogen-containing titanium carbide TiC_x .

Figure 1 shows a neutron diffraction pattern of a $\text{TiC}_{0.50}\text{H}_{0.22}$ sample with a well-defined incoherent background, which declines as the Wulf–Bragg angle increases (with respect to the dashed horizontal line). This type of background in a neutron diffraction pattern is intrinsic to hydrogen atoms only [6]. This is a qualitative confirmation of the occurrence of hydrogen in the sample. Other nonstoichiometric titanium carbide samples have similar neutron diffraction patterns. In stoichiometric $\text{TiC}_{1.00}$ and near-stoichiometric $\text{TiC}_{0.97}$ which are free of hydrogen, an incoherent background does not appear with increasing Bragg angle in neutron diffraction patterns. Neutron diffraction shows that the crystal structure in all samples can be described in terms of space group $Fm\bar{3}m$ and all samples, but $\text{TiC}_{1.00}$ and $\text{TiC}_{0.97}$, contain hydrogen in their crystal lattices. In this model, carbon atoms are

randomly distributed over octahedral interstices $4b$ and hydrogen atoms are in tetrahedral interstices $8c$ (Table 2).

Our results match with the earlier reported high-temperature ($T \geq 1200^\circ\text{C}$) metalloid distribution in $\text{TiC}_{0.50}\text{H}_{0.21}$ and $\text{TiC}_{0.47}\text{H}_{0.21}$ lattices [3]. The hydrogen content in the lattice of nonstoichiometric titanium carbide TiC_x increases linearly as the defect content of the carbon sublattice increases (as the carbon concentration decreases) (Fig. 2). This trend may be explained in the following manner. According to Latergaus et al. [8], there are repulsing forces between carbon and hydrogen atoms in the interstices of the TiC_xH_y crystal lattice. Tetrahedral interstices in the FCC lattice at high temperatures are energetically favorable for hydrogen atoms [9]. Some hydrogen is evolved from the precursor powder mixtures under high burning temperatures, and the thus-formed product is further hydrated during cooling [10]. The higher the carbon concentration (the lower the carbon defect concentration), the stronger the repulsion between the extant carbon atoms occurring in lattice and the incorporating hydrogen atoms. Further, the inward hydrogen diffusion is hindered the more strongly, the lower the carbon defect concentration in the TiC_x lattice. Thus, the highest amount of hydrogen atoms is observed in the TiC_xH_y lattice with the highest carbon defect concentration.

Figure 3, a shows unit cell parameter a versus concentration curves for FCC TiC_x [11] and for the FCC TiC_xH_y under study. One can infer from Fig. 3 that the two FCC alloys have similar unit cell versus concentration curves. In both cases, the parameter a first rapidly increases with increasing carbon concentration (with a high slope), and then the increase slows down.

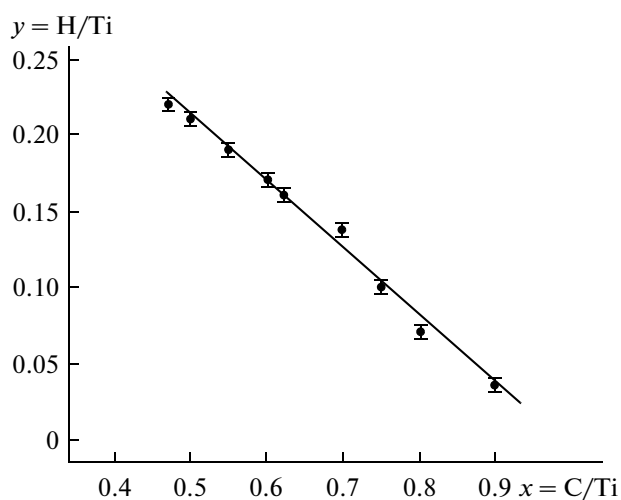


Fig. 2. Hydrogen impurity content versus carbon index in TiC_x .

Table 2. Structural characteristics of titanium carbohydride $\text{TiC}_{0.50}\text{H}_{0.22}$ quenched from 1475 K

Atom	Position	$B_i \pm 0.001, \text{nm}^2$	n	Δn
Ti	$4a$	0.005	4	
C	$4b$	0.004	2	0.03
H	$8c$	0.004	0.88	0.03
$R, \%$	$R_p = 3.8; R_{wp} = 5.0; R_{Br} = 4.3$			

B_i stands for an individual thermal factor; R_p , R_{wp} , and R_{Br} are divergence factors for the full neutron diffraction profile, point weights, and Bragg peak intensities, respectively; and n is the number of atoms.

This trend may be due to the following: as the carbon concentration approaches the Ti_1C_1 stoichiometry, statistic distortions of the crystal lattice become progressively smaller and the interplay of the metal–metal and metal–carbon interactions becomes more stable (the carbon–carbon bonding is regarded as very weak).

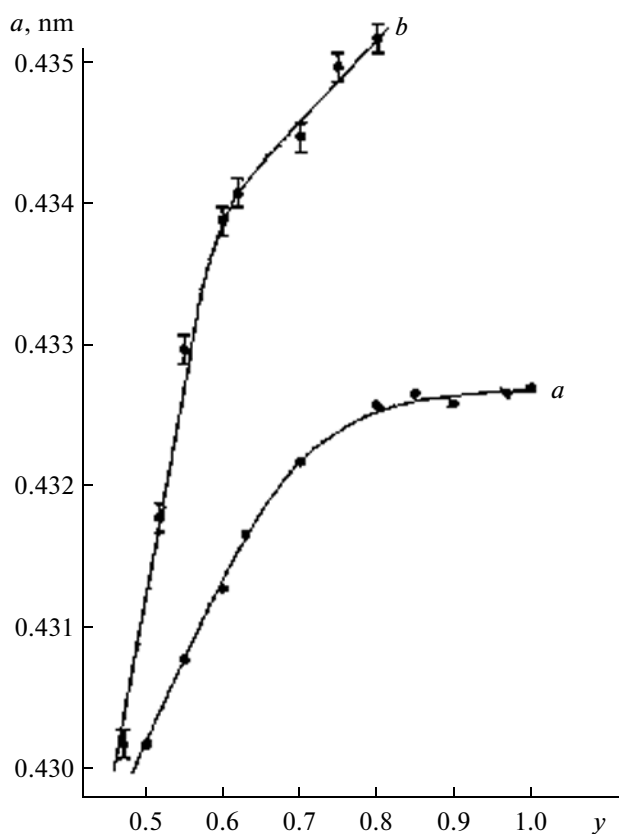


Fig. 3. Unit cell parameter a versus concentration for (a) pure titanium carbide TiC_x [11] and (b) titanium carbohydride TiC_xH_y .

Judging from the TiC_xH_y unit cell versus concentration curve (Fig. 3, *b*), that trend persists in the presence of hydrogen. Noteworthy here is a stronger effect of a small hydrogen concentration (within 0.38 wt %) on the unit cell parameter.

Therefore, we may infer that the hydrogen concentration in the TiC_x lattice within 0.38 wt % has no appreciable effect on the character of interatomic interactions in the homogeneity region, but generates strong internal strain in the lattice. As a result, the unit cell parameter a increases appreciably, and this increase becomes greater in response to increasing carbon concentration. This trend is likely to be due to increasing internal strain in response to increasing repulsive strength between hydrogen and carbon atoms caused by increasing carbon concentration.

In summary, we have shown that powdery titanium containing minor hydrogen can serve as a precursor for self-propagating synthesis to produce hydrogen-containing titanium carbide TiC_x not only of stoichiometric (near-stoichiometric) composition. The hydrogen concentration in the TiC_x lattice increases linearly with deviation from stoichiometry. Hydrogen at levels of ≤ 0.38 wt % in the FCC lattice of nonstoichiometric titanium carbide TiC_x appreciably increases the unit cell parameter without affecting its concentration dependence. As a result, it becomes possible to determine the hydrogen impurity in titanium carbide from the unit cell versus concentration curve.

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