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PHYSICAL METHODS OF INVESTIGATION

Neutron Diffraction Study of Dehydrogenation of Titanium Carbohydrides TiC_xH_y

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Abstract—The possibility of the synthesis of hydrogen-nonstoichiometric cubic titanium carbide TiC_x of high purity from powdery nonstoichiometric cubic titanium carbohydride TiC_xH_y or nonstoichiometric titanium carbide with admixture hydrogen by annealing in a continuously maintained vacuum of no worse than 1.33×10^{-3} Pa at temperatures of 600–750°C for several hours has been shown. Similar annealing at higher temperatures ($T \geq 800$°C) does not lead to the complete removal of hydrogen from a sample due to intensive sintering. In this case, it seems that pores between sintered particles are hydrogen traps, and the release of hydrogen through the surface of sintered particles is hindered.

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Face-centered cubic (FCC) titanium carbide of variable composition TiC_x is widely used in the hard alloy industry [1]. In recent times, nonstoichiometric titanium carbide TiC_x ($x = 0.50$–0.80) has found wide application in medicine due to its resistance to a biological medium, nontoxicity and non-carcinogenicity, resistance to fatigue damages, the absence of corrosion phenomena, the possibility to acquire an elasticity modulus close to the bone tissue values, and low primary costs [2].

TiC_x coatings are used for a cardiovascular kit [3]. A sample becomes two phases at $x < 0.50$ [4] and brittle at $x > 80$ [5]. Nonstoichiometric titanium carbide $TiC_{0.50-0.80}$ can "coexist" with a living organism for a long time (is biocompatible), so it is used in the manufacture of implants. However, the synthesis of pure nonstoichiometric titanium carbide is problematic, as its crystal structure contains many vacancies in the carbon sublattice. The homogeneity region of the FCC TiC_x phase lies within a concentration range of $0.50 \leq x < 1.00$ (the stoichiometric composition is $x = 1$) [4]. Correspondingly, a nonstoichiometric FCC TiC_x phase can have a great number of structural vacancies, namely, octahedral interstices, which are free from carbon atoms, represent perfect traps for hydrogen atoms, in a concentration that can reach 50 at % at the lower limit of the homogeneity region of nonstoichiometric titanium carbide. Almost all of the existing physicochemical methods for the synthesis of titanium carbide are based on the use of either titanium powders, which frequently contain admixture hydrogen, or a hydrogen-containing medium [1, 6]. Hydrogen atoms are incorporated into free interstices in the crystal lattice of nonstoichiometric FCC titanium carbide, where the repulsive forces of carbon atoms do not act. As a result, the final nonstoichiometric titanium carbide product contains some amount of hydrogen. The higher is the concentration of carbon vacancies in nonstoichiometric titanium carbide, the greater is the content of hydrogen in it [7]. In engineering, this fact is ignored. However, even a small admixture of hydrogen (H/Ti = 0.23 wt %) strongly worsens the physical and chemical properties of the material [8, 9]. The "hydrogen brittleness" effect is well known. For this reason, the use of nonstoichiometric TiC_x for practical purposes faces the challenge of its dehydrogenation to a high degree of purity with respect to hydrogen. The objective of this work is to perform the neutron diffraction study of the dehydrogenation of powdery nonstoichiometric titanium carbohydrides TiC_xH_y or nonstoichiometric titanium carbides containing admixture hydrogen for the synthesis of nonstoichiometric titanium carbides of high purity with respect to hydrogen.

EXPERIMENTAL

In this work, we used FCC titanium carbohydrides TiC_xH_y (NaCl structural type), which were studied earlier [7], to elucidate the arrangement of embedded atoms in interstices of the FCC lattice of the titanium matrix. Titanium carbohydride samples ($TiC_{0.50}H_{0.21}$, $TiC_{0.55}H_{0.19}$, $TiC_{0.60}H_{0.17}$, $TiC_{0.62}H_{0.17}$, $TiC_{0.70}H_{0.14}$, $TiC_{0.75}H_{0.10}$, and $TiC_{0.80}H_{0.08}$) were prepared by self-propagating high-temperature synthesis [6] from carbon powders (specialty grade) and titanium powder

(PTM grade; 98.92 wt %; 0.38 wt % admixture hydrogen content). The contents of carbon and hydrogen in the samples were determined by chemical analysis in the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences. To determine the hydrogen concentration, sample portions were burnt in an oxygen flow with further weighing of the water formed upon combustion. The concentration of carbon atoms in the samples was also determined by burning a sample portion with absorption of the formed CO_2. The measurement error was ±0.3%.

The dehydrogenation of titanium carbohydrides TiC_xH_y was performed at various temperatures within a range of 1200–600°C in an SShVL-type vacuum furnace. To dehydrogenate samples in the form of a free-flowing crystalline powder, they were freely poured into a silica ampoule. They represented a mixture of solid particles appressed to each other under their own weight with various shapes and sizes ($r \approx 40–60$ μm). A vacuum of no worse than 5.33×10^{-3} Pa was maintained in the working volume of the furnace in the continuous evacuation mode during the dehydrogenation. The dehydrogenation time was no less than 24 h at each temperature. The minimum time of exposure for at some temperature was selected to be 24 h under the assumption that this time will sufficient for equilibrium dehydrogenation at each temperature. However, the time required for the complete dehydrogenation of powder titanium carbohydrides TiC_xH_y depends on the amount of the dehydrogenated sample, the size of powder particles, and the content of hydrogen in the sample. Hence, the dehydrogenation time should be specially selected in each case and can also be shorter than 24 h.

The particle sizes of the dehydrogenated powders were 40–60 μm, and their total masses were ~14–20 g. If the samples represented sintered alloys, it was necessary to grind them in an agate or ceramic mortar or in an agate ball mill for dehydrogenation. By the way, titanium carbohydrides are very brittle in contrast to titanium carbides. For this reason, their grinding does not present any difficulty. From the viewpoint of powder metallurgy, this operatio is not superfluous, as the manufacturing of billets and articles from different metals and alloys require them to be milled into powder [10].

After dehydrogenation at each temperature, a neutron diffraction pattern was recorded, and the content of hydrogen in the sample was qualitatively traced by a decrease in the noncoherent background in the neutron diffraction patterns with an increase in the Wulf–Bragg angle due to the noncoherent scattering of neutrons on hydrogen atomic nuclei. Such a character of the background in a neutron diffraction pattern is specific only to hydrogen atoms due to great amplitude of the noncoherent scattering of thermal neutrons on hydrogen atom nuclei [11]. The content of hydrogen in dehydrogenated samples was also determined by minimizing the unreliability factors for the characterization of their crystal structure by the full-profile analysis of a neutron diffraction pattern. The neutron diffraction patterns of samples were recorded on a DN-500 neutron diffractometer installed on the thermal column of a WWR-SM nuclear reactor at the Institute of Nuclear Physics of the Academy of Sciences of Uzbekistan ($\lambda = 0.1085$ nm).

Neutron diffraction enables the content and location of hydrogen atoms and light elements in the crystal lattice of titanium carbohydride TiC_xH_y to be reliably determined due to comparable absolute values of the coherent scattering of neutrons (b) on metal and nonmetal atomic nuclei ($b_{Ti} = -0.34 \times 10^{-5}$ nm, $b_C = 0.665 \times 10^{-5}$ nm, $b_H = -0.3745 \times 10^{-5}$ nm [11]). The calculation of neutron diffraction patterns was performed via full-profile Rietveld analysis using the DBW 3.2 software [12]. The ratio of absolute neutron coherent scattering amplitudes and the full-profile Rietveld analysis of a neutron diffraction pattern give low estimation errors for the content of hydrogen in the lattice (no higher than 0.01 of atomic ratio).

X-ray diffraction was used to evaluate the single-phase constitution and homogeneity of samples. X-ray diffraction pattenrs were recorded on a DRON-3M X-ray diffractometer (CuK_α radiation, $\lambda_{av} = 0.5418$ nm, Ni filter). At first, the survey pattern was taken within a 2θ angle range of 10°–110° at a detector revolution speed of 1 deg/min. These spectra were used to establish the phase composition of samples. Measurements within a narrow diffraction peak range at a detector revolution speed of 1/4 deg/min and $2\theta > 101°$ were used to determine the unit cell parameters. According to X-ray diffraction analysis results, the studied samples after homogenizing annealing at 1200°C in an evacuated and sealed silica ampoule for 6 h and further quenching in water were homogeneous single phases and had a NaCl type FCC lattice with a (space group $Fm3m$). The unit cell parameters of samples are given in [7] ($a = 0.4301–0.4351$ nm).

RESULTS AND DISCUSSION

Nonstoichiometric titanium carbides $TiC_{0.47}$, $TiC_{0.50}$, $TiC_{0.55}$, $TiC_{0.60}$, $TiC_{0.62}$, $TiC_{0.70}$, $TiC_{0.75}$, and $TiC_{0.80}$ were synthesized by dehydrogenation of free-flowing powders of corresponding titanium carbohydrides within a temperature range of 1200–600°C in 50 or 100°C steps at a certain time of exposure at each temperature (table). After dehydrogenation at each temperature, the neutron diffraction pattern of the sample was recorded.

The neutron diffraction pattern of the initial titanium carbohydride $TiC_{0.50}H_{0.21}$ is shown in Fig. 1, spectrum a. Neutron diffraction analysis confirms the results of X-ray diffraction analysis. As can be seen from Fig. 1, spectrum a, the neutron diffraction pat-

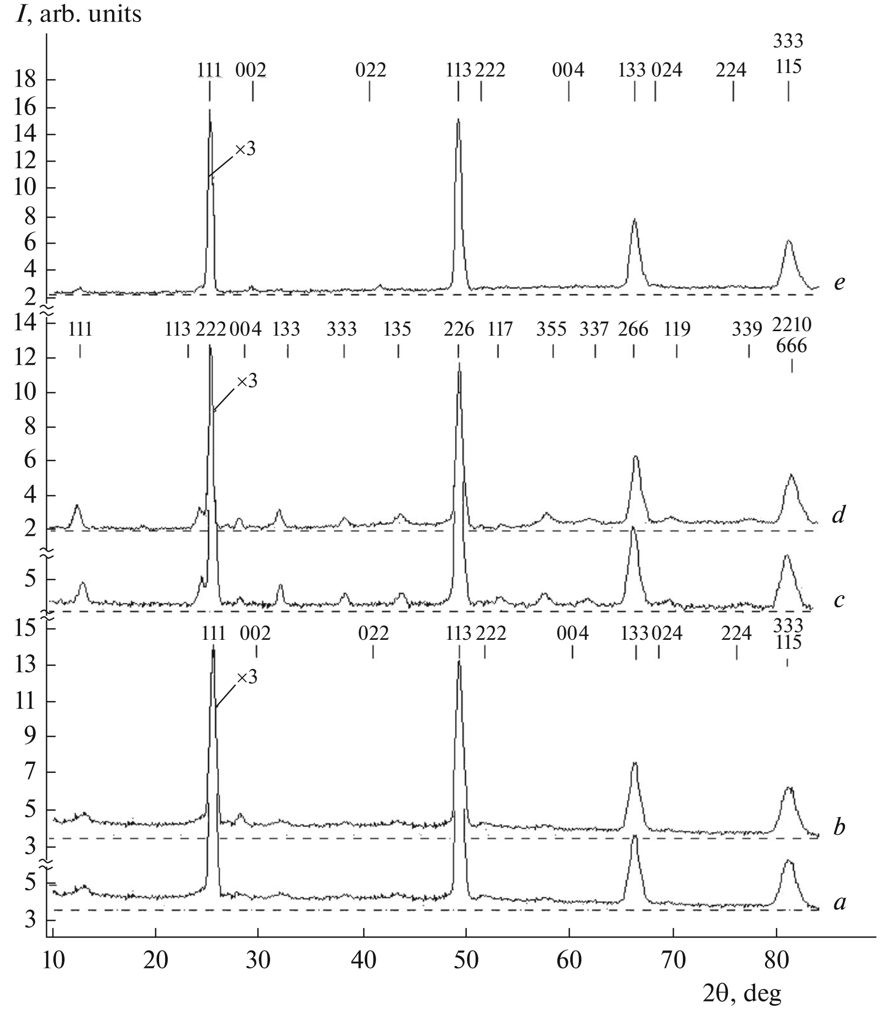

Fig. 1. Neutron diffraction patterns of $TiC_{0.50}H_{0.21}$: (*a*) initial, (*b*) after annealing in an open ampoule in a vacuum furnace at a temperature of 1200°C for 50 h, (*c*) after stepped annealing in a vacuum furnace at 1200 + 1000 + 600°C for 100 h at each temperature and (*d*) in a vacuum furnace at 600°C for 24 h. Miller indices above the reflections are given within the framework of corresponding space groups: (*a*), (*b*), (*e*) *Fm*3*m*, (*c*), (*d*) *Fd*3*m*. Horizontal dashed lines indicate the character of the background in the neutron diffraction pattern.

tern can be indexed in space group *Fm*3*m*. The neutron diffraction patterns of the other samples are the same as for $TiC_{0.50}H_{0.21}$. According to neutron diffraction analysis, the crystal structure of all the samples quenched from 1200°C can be described in space group *Fm*3*m*, where carbon atoms randomly occupy octahedral interstices 4(*b*) in the FCC matrix lattice (positions 4(*a*)) and hydrogen atoms occupy tetrahedral interstices 8(*c*). This result agrees with the data [7] on the distribution of nonmetals over the TiC_xH_y lattice at high temperatures.

As can be seen from Fig. 1, spectrum *a*, the neutron diffraction pattern has a pronounced noncoherent background descending with an increase in the Wulf–Bragg angle. This qualitatively confirms the existence of hydrogen in the sample [11]. Neutron diffraction analysis indicates that the H/Ti atomic ratio in the lattice is 0.21, which corresponds to the result of chemical analysis. To remove hydrogen atoms from the lattice, annealing was first performed in an open silicaampoule in a vacuum furnace at 1200°C for 50 h in the continuous evacuation mode. As can be seen from Fig. 1, spectrum *b*, a noncoherent background and the same structural type (space group *Fm*3*m*) are retained in the neutron diffraction pattern after such annealing. The calculation of the neutron diffraction pattern by the Rietveld method shows that the same distribution character of interstitial atoms and the atomic ratio H/Ti = 0.21 are also retained in this case. Under such the assumptions, the least factor of unreliability in the characterization of a structure by Bragg maxima was obtained ($R_{\text{Bragg}} = 2.5\%$). The results of neutron diffraction analysis for hydrogen in the samples before and after annealing in different modes are given in the table.

Hydrogen concentration, crystal structure (space group), unit cell parameters, and Rietveld structure characterization unreliability factors for FCC titanium carbohydrides TiC_xH_y before and after dehydrogenation in different modes*

Sample	Annealing temperature, °C, annealing time	Concentration, x = H/Ti	Space group	a, nm	R_{Bragg}, %
$TiC_{0.50}H_x$	Initial	0.21	*Fm*3*m*	0.4301	2.5
	1200, 30 h	0.21	*Fm*3*m*	0.4301	2.5
	1200–1000–600, 100 h each	0.11	*Fd*3*m*	0.8632	4.2
	800, 24 h	0.06	*Fm*3*m*	0.4301	3.6
	750, 24 h	0	*Fm*3*m*	0.4301	2.7
	600, 24 h	0	*Fd*3*m*	0.8660	3,9
	600, 24 h	0	*Fm*3*m*	0.4293	3.1
$TiC_{0.50}H_{0.21}$	Initial	0.21	*Fd*3*m*	0.8660	4.2
	600, 24 h	0	*Fd*3*m*	0.8651	5.4
	550, 24 h	0	*Fd*3*m*	0.8651	5.4
$TiC_{0.70}H_{0.14}$	Initial	0.14	*Fm*3*m*	0.4343	5.2
	800, 24 h	0	*Fm*3*m*	0.4337	3.1
	700, 24 h	0	*Fm*3*m*	0.4337	2.3

* *Fm*3*m* and *Fd*3*m* correspond to nonordered and ordered FCC structures, respectively. R_{Bragg} is the factor of unreliability in the characterization of a crystal structure by Bragg maxima.

Stepped annealing was further performed in open silica ampoules in a continuously evacuated furnace at 1200 + 1000 + 600°C for 100 h at each temperature. In this case, some superstructural reflections corresponding to space group *Fd*3*m* appeared in the neutron diffraction pattern. It is noteworthy that, as follows from the results [13], the carbon and hydrogen atoms in titanium carbohydride $TiC_{0.50}H_{0.21}$ become ordered at 600°C, and the crystal structure of the sample can be described in space group *Fd*3*m*, i.e., becomes an ordered FCC lattice with the unit cell parameter $a \approx 2a_0$, where a_0 is the parameter of the initial FCC lattice. A noncoherent background in the neutron diffraction pattern still persists (Fig. 1, spectrum *c*). According to neutron diffraction analysis, the atomic ratio C/Ti = 0.11 in the sample is retained (table). Hence, if annealing is started at high temperatures (1200°C), hydrogen is not completely removed from the lattice of interstitial alloys under subsequent low-temperature annealings in a continuously evacuated even for several days (Fig. 1, spectrum *c*).

The retention of hydrogen in the lattice is caused by the following: as shown by our experiments, the sample is sintered at temperatures ≥800°C: the free-flowing powder, which has been freely poured into an ampoule, is converted after high-temperature annealings into a hardened rod, which has a porosity of 60–70% and takes the cylindrical shape of the ampoule.

The porosity of the sintered sample P was determined by the formula

$$P = (\rho_{X\text{-ray}} - \rho_{exp})/\rho_{X\text{-ray}},$$

where $\rho_{X\text{-ray}}$ is the X-ray density and ρ_{exp} is the experimentally observed density.

Hence, it is possible to make a conclusion that the sintering of a powder sample prevents removal of hydrogen from its lattice upon annealings. Further, the $TiC_{0.50}H_{0.21}$ sample was annealed at 800°C for 24 h. The porosity of the sample at this temperature was 80%. According to neutron diffraction analysis, the atomic ratio C/Ti = 0.06 was retained in the sample after such annealing.

Further, the initial sample was annealed in a vacuum furnace in the continuous evacuation mode at 600°C for 24 h. The sample retained its flowability at this temperature. According to the neutron diffraction pattern, a noncoherent background disappears from the sample it after such annealing, thus qualitatively indicating the absence of hydrogen in the sample (Fig. 1, spectrum *d*, table). The background in the neutron diffraction pattern grows with an increase in the Wulf–Bragg angle in contrast to the neutron diffraction pattern of the hydrogen-containing sample, and the formation of an ordered phase describable in space group *Fd*3*m* is observed in this case. Chemical and neutron diffraction analyses show that, really, no hydrogen remains in the sample under these treatment conditions. Similar results were obtained after annealing of the initial $TiC_{0.50}H_{0.21}$ sample at 700 and 750°C for 24 h (table). When it is necessary to obtain nonordered titanium carbide (with a structure describable in space group *Fm*3*m*), ordered titanium carbide synthesized at 600 or 700°C must be annealed at 1000°C for ~5 h. The neutron diffraction pattern of this sample is shown in Fig. 1, spectrum *e*. The powder sample fails to appreciably sinter in 5 h. At the same time, 5 h are sufficient for the ordered phase to become completely disordered. Similar results were obtained for titanium carbohydrides $TiC_{0.55}H_{0.21}$–$TiC_{0.80}H_{0.08}$ (Fig. 2). It is noteworthy that the dehydrogenation of titanium carbohydride TiC_xH_y with a relatively high carbon con-

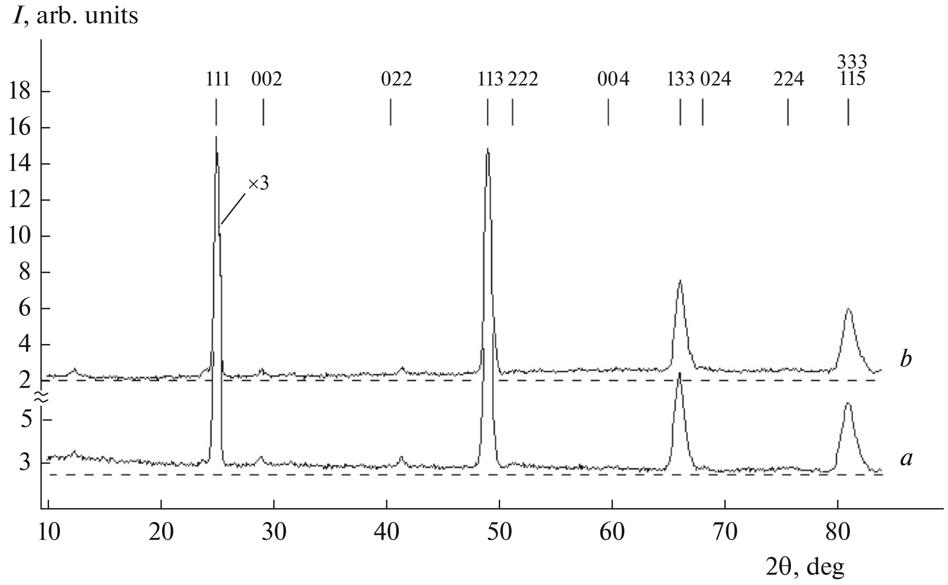

Fig. 2. Neutron diffraction patterns of (*a*) initial titanium carbohydride $TiC_{0.70}H_{0.14}$ and (*b*) after annealing at 700°C for 24 h.

tent ($x \geq 0.70$) can be performed even at 800°C, at which no appreciable sintering of samples is observed.

The obtained results can be explained as follows. Two competing processes, such as sintering and dehydrogenation, simultaneously occur in powder samples under annealing. The higher is the temperature of annealing in a vacuum and the number of carbon vacancies in a lattice, the more intensive is the sintering process. The sintering of a powder hinders the escape of hydrogen from a sample: the boundaries between sintered grains prevent its release from a lattice. A high sintering degree is observed for $TiC_{0.47}H_{0.21}$–$TiC_{0.60}H_{0.21}$ at a temperature ≥800°C and, correspondingly, dehydrogenation is hindered. In this case, a hydrogen-containing interstitial alloy is formed. At $750°C \geq T \geq 600°C$, sintering is appreciably inhibited in the samples of such a composition, as indicated by the state of the powder after annealing. At the same time, the mentioned temperatures are sufficient for the diffusion of hydrogen and its escape from the lattice. The lower is the concentration of structural vacancies (the higher is the carbon concentration), the more hindered is the process of sintering due to a decrease in the diffusion rate of atoms. For this reason, the degree of sintering in the samples $TiC_{0.70}H_{0.21}$–$TiC_{0.80}H_{0.08}$ with a high carbon content at 800°C is still rather small and, by virtue of this fact, their complete dehydrogenation can be observed at this temperature.

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