

Hydrogen Accumulation and Distribution during the Saturation of a VT1-0 Titanium Alloy by an Electrolytic Method and from a Gas Atmosphere

V. N. Kudiyarov*, A. M. Lider, N. S. Pushilina, and N. A. Timchenko

National Research Tomsk Polytechnical University, ul. Lenina 30, Tomsk, 634050 Russia

*e-mail: viktor.kudiyarov@gmail.com

Abstract—The accumulation, distribution, and thermally stimulated release of hydrogen in a VT1-0 titanium alloy during electrolytic saturation and gas-phase saturation are studied. After electrolytic saturation, a 0.4- μm -thick surface layer consisting of δ hydrides with a binding energy of 108 kJ/mol forms in the alloy. The hydride dissociation after electrolytic saturation in heating occurs in the temperature range 320–370°C. After saturation from a gas atmosphere, δ hydrides with a binding energy of 102 kJ/mol form throughout the alloy volume. The dissociation of the hydrides formed during gas-phase saturation in heating occurs in the temperature range 520–530°C. A further increase in the temperature is accompanied by the transformation of titanium from the α into the β modification. At 690–720°C, the phase transformation is completed, and another hydrogen desorption peak appears in a thermally stimulated hydrogen desorption spectrum.

1. INTRODUCTION

Titanium and its alloys are widely used as structural materials in various industries [1–5]. The penetration and accumulation of hydrogen in titanium parts change their physicochemical and service properties and cause their delayed fracture because of hydrogen embrittlement [6]. The kinetics and intensity of such changes depend on the state of hydrogen in a material [7]. Hydrogen in titanium can be in the form of hydrides or in a dissolved state [8, 9]. To determine the quantity, distribution, and state of accumulated hydrogen at various types of treatment is necessary to develop methods for preventing hydrogen embrittlement.

To determine the state and quantity of hydrogen accumulated in metals, researchers apply thermodesorption spectroscopy (TDS), where the flow of desorbed hydrogen is continuously measured in heating at a given rate [10, 11]. In the TDS studies of hydrogen accumulation in titanium alloys, it is important to take into account the effect of the phase transitions in the titanium–hydrogen system on thermally stimulated hydrogen desorption, since they affect the shape of TDS spectra [8, 12]. The hydrogen accumulation in titanium was analyzed by TDS in many works [8–12]. For example, the effect of the phase transitions in the titanium–hydrogen system on the thermally stimulated hydrogen desorption after electrolytic hydrogen saturation was comprehensively studied in [12]. The authors of [9, 10] investigated the hydrogen accumulation in titanium by TDS during saturation from a gas atmosphere; however, they did not analyze the effect

of the phase transitions in the titanium–hydrogen system on thermally stimulated hydrogen desorption after saturation from a gas atmosphere.

To understand the processes of hydrogen accumulation in titanium alloys, one has to know detailed information on the phase transitions in the titanium–hydrogen system during simultaneous thermal action and hydrogen desorption. Such information can be obtained from the diffraction data measured during TDS experiments using synchrotron radiation. The purpose of this work is to study the hydrogen accumulation and distribution in a commercial-purity titanium alloy (VT1-0) during electrolytic saturation and saturation from a gas atmosphere and to perform in situ investigations of the effect of the phase transitions in the titanium–hydrogen system on the thermally stimulated hydrogen desorption using synchrotron radiation.

2. EXPERIMENTAL

For investigations, we prepared $20 \times 20 \times 1$ -mm samples. They were spark-cut from a VT1-0 titanium alloy sheet in the as-delivered state. The sample surfaces were mechanically polished to remove a surface oxide film. The samples were vacuum annealed at 750°C for 60 min to remove defects and to relieve surface stresses.

Electrolytic saturation was performed in an M-solution of sulfuric acid for 360 min at an electric current of 0.73 A and an electrolyte temperature of 70°C. Saturation from a gas atmosphere was carried out at a

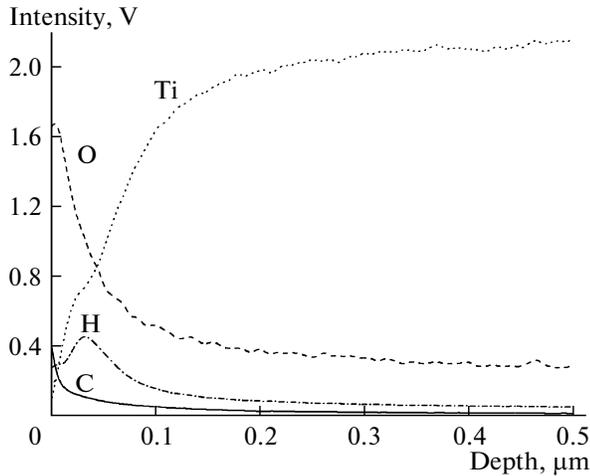


Fig. 1. Depth profiles of the elements in the titanium alloy before hydrogen saturation.

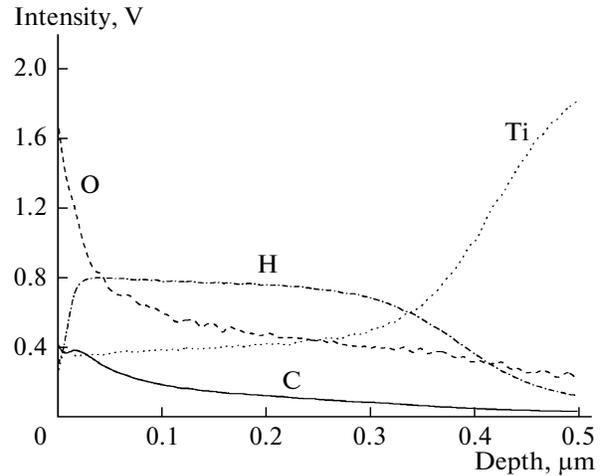


Fig. 2. Depth profiles of the elements in the titanium alloy after electrolytic hydrogen saturation.

temperature of 600°C for 60 min at a hydrogen pressure of 6.6×10^4 Pa in the chamber of a computer-assisted Gas Reaction Controller LPB setup [13]. After hydrogen saturation, we measured the hydrogen concentration with an RHEN 602 (LECO) hydrogen analyzer. The depth profiles of hydrogen were recorded using a GD-Profilier 2 (Horiba) glow discharge plasma spectrometer [14]. The phase composition and the structure parameters of the samples after saturation were studied on an XRD-6000 diffractometer using $\text{CuK}\alpha$ radiation. The phase composition was analyzed using the PCPDFWIN and PDF-4+ databases and the POWDER CELL 2.5 full-profile analysis software package.

The spectra of the thermally stimulated hydrogen desorption from the samples were recorded on a computer-assisted Gas Reaction Controller LPB setup using an RGA 100 (Stanford Research Systems) quadrupole mass spectrometer. A sample was placed in a chamber pumped down to a pressure below 10^{-4} Pa and was then linearly heated. The hydrogen flow was continuously measured with the mass spectrometer. The heating rate of a sample during TDS was 4–8 °C/min and the heating range was 30–900°C. The spectra of thermally stimulated hydrogen release were analyzed by the Kissinger method [15].

The in situ investigation of the phase transitions in the titanium–hydrogen system during thermally stimulated hydrogen release was performed on the Precision X-ray Diffraction II Station of the Institute of Catalysis, Siberian Branch, Russian Academy of Sciences in synchrotron radiation channel 6 of the VEPP-3 electron storage ring [16, 17]. This station is characterized by an OD-3M one-coordinate detector used in the powder diffractometer. The detector consists of a multiwire proportional gas chamber, a detecting unit with a coordinate processor, and a computer [18]. The one-coordinate detectors record scattered

radiation in a certain angular range ($\sim 30^\circ$) in 3328 channels at a speed of response up to 10 MHz. A sample was placed in the chamber pumped down to a pressure below 10^{-4} Pa and was then linearly heated in the range 30–750°C at a rate of 6 °C/min. X-ray diffraction patterns were recorded every heating minute, i.e., every 6°C. The recorded X-ray diffraction patterns were processed and analyzed using the PDF-2-search-match, FullProf, and Crystallographica software packages.

3. RESULTS AND DISCUSSION

3.1. Hydrogen Accumulation and Distribution

Figures 1–3 show the depth profiles of the elements in titanium alloy samples before and after hydrogen saturation. Oxide compounds and gaseous impurities

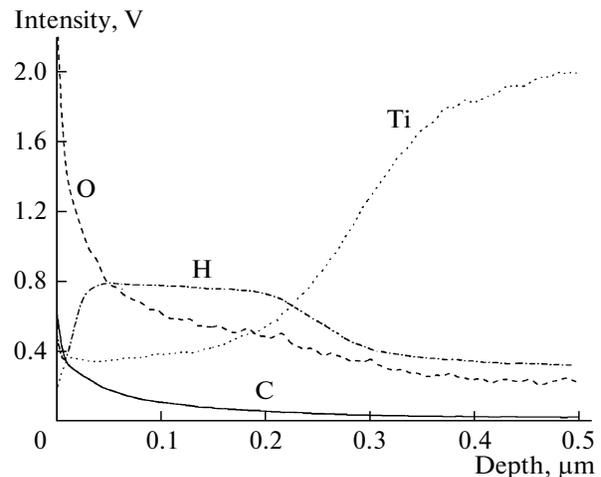


Fig. 3. Depth profiles of the elements in the titanium alloy after gas-phase hydrogen saturation.

XRD results for the titanium alloy

Samples	Detected phases	Phase content, vol %	Lattice parameters, 0.1 nm
Initial	Ti_hexagonal	99.9 ± 0.1	$a = 2.941; c = 4.668$
Electrolytic saturation	Ti_hexagonal	11.1 ± 0.1	$a = 2.917; c = 4.633$
	TiH ₂ _cubic	88.9 ± 0.6	$a = 4.3544$
Gas-phase saturation	Ti_hexagonal	59 ± 0.5	$a = 2.936; c = 4.665$
	TiH ₂ _cubic	40.26 ± 0.3	$a = 4.3846$

(carbon, hydrogen) are present in a 0.1- μm -thick surface layer. In the initial titanium alloy, hydrogen exists in a thin surface region and its absolute content is 0.0034 wt %.

A 0.4- μm -thick layer with a high hydrogen content forms in samples as a result of electrolytic hydrogen saturation (Fig. 2). In this case, the signal intensity of hydrogen is approximately twice as high as the signal intensity of titanium, and an analysis of the depth profile of hydrogen suggests that the layer consists of titanium hydride with a composition close to stoichiometric composition TiH₂. The depth profiles of hydrogen in titanium alloy samples after saturation from a gas atmosphere are characterized by the fact that the hydrogen level remains high across the entire analysis depth (3 μm), and the hydride layer thickness is 0.25 μm . This finding is explained by the fact that, during electrolytic saturation, hydrogen accumulates in titanium in the near-surface layer and weakly diffuse deep into the sample volume because of the low diffusion coefficient of hydrogen in titanium at moderate temperatures [7]. During hydrogen saturation from a gas atmosphere at high temperatures, hydrogen diffuses deep into the sample volume and is distributed over the entire sample volume at a sufficient saturation time. The absolute hydrogen content was 0.966 wt %

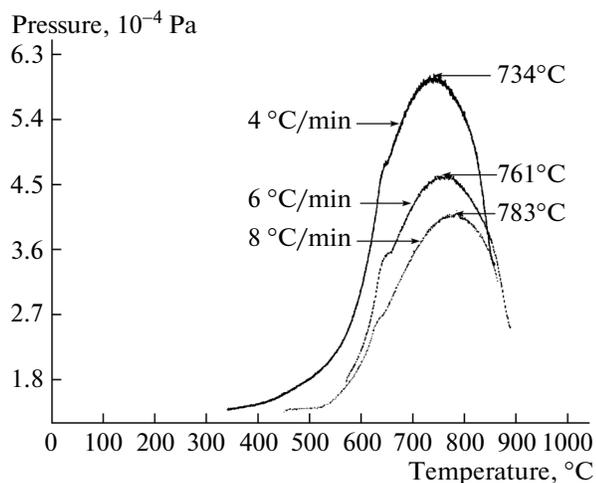


Fig. 4. Spectra of thermally stimulated hydrogen desorption from the titanium alloy after electrolytic saturation.

in the samples saturated from a gas atmosphere at 600°C and 0.0241 wt % in the samples subjected to electrolytic saturation.

3.2. Effect of Hydrogen on the Phase Composition of the Titanium Alloy

The results of X-ray diffraction (XRD) analysis of the effect of hydrogen saturation on the phase composition of the titanium alloy are given in the table.

During electrolytic saturation, hydrogen accumulates in the near-surface layer of the samples and forms hydride phases, the compositions of which are close to the stoichiometric composition, with the titanium alloy (Fig. 2). This follows from the XRD results (see the table). Hydrogen saturation from a gas atmosphere at a high temperature is accompanied by hydrogen diffusion without the formation of hydride phases [12]. Upon cooling after saturation, hydrides form in the samples; however, the volume content of hydrides on the surfaces of the samples saturated from a gas atmosphere is lower than that of hydrides at the surfaces of the samples subjected to electrolytic saturation (see the table).

3.3. Thermally Stimulated Hydrogen Desorption

The spectra of thermally stimulated hydrogen desorption from titanium alloy samples are shown in Fig. 4 (electrolytic saturation) and Fig. 5 (gas-phase saturation). As was detected earlier, the absolute hydrogen content in the samples saturated from a gas atmosphere is higher than in the samples subjected to electrolytic saturation. Thus, the intensity of hydrogen release from the samples saturated from a gas atmosphere (increase in the pressure from 1×10^{-3} to 2×10^{-2} Pa) is two orders of magnitude higher than that from the samples subjected to electrolytic saturation (increase in the pressure from 1.8×10^{-4} to 6.2×10^{-4} Pa).

The binding energy of hydrogen for each saturation method was determined from the dependences of $\ln(\beta/T^2)$ on $1/T$, where β is the heating rate and T is the peak temperature (Fig. 6) [10]. As a result, we obtained the following binding energies of hydrogen: 108 kJ/mol for electrolytic saturation and 102 kJ/mol for gas-phase saturation. These data agree with the

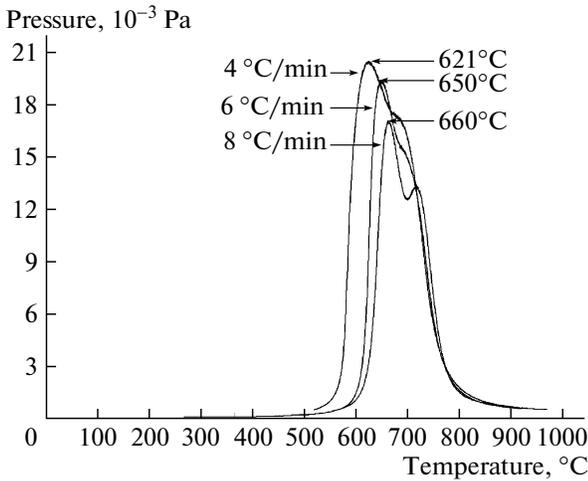


Fig. 5. Spectra of thermally stimulated hydrogen desorption from the titanium alloy after gas-phase saturation.

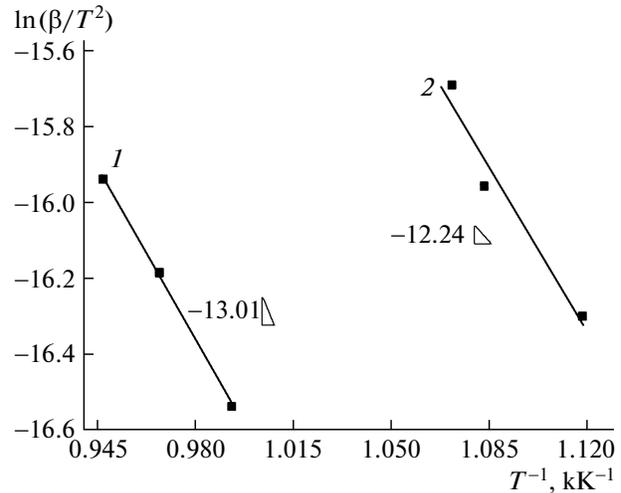


Fig. 6. $\ln(\beta/T^2)$ vs. $1/T$ for (1) electrolytic saturation and (2) gas-phase saturation.

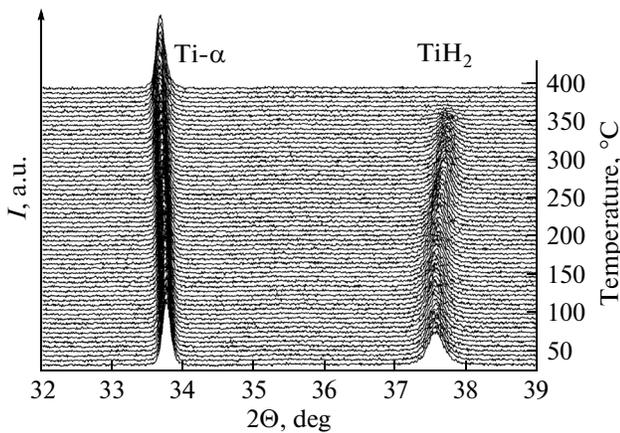


Fig. 7. Kinetics of the phase transitions in heating of the titanium alloy after electrolytic hydrogen saturation.

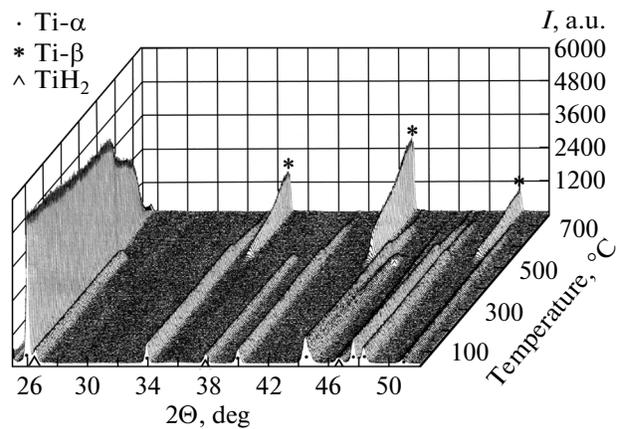


Fig. 8. Kinetics of the phase transitions in heating of the VT1-0 titanium alloy after gas-phase hydrogen saturation.

results [12, 19] on determining the binding energy of hydrogen in a titanium alloy after electrolytic saturation (108 and 106 kJ/mol) and gas-phase saturation (100 kJ/mol). This binding energy range for hydrogen in titanium corresponds to hydride, which agrees with our XRD data.

The TDS spectra of the samples saturated from a gas atmosphere are characterized by the appearance of a second peak in the high-temperature region, which is related to phase transitions in the titanium–hydrogen system.

3.4. Phase Transitions in the Titanium–Hydrogen System during Thermally Stimulated Hydrogen Desorption

Figure 7 shows the X-ray diffraction patterns that demonstrate the kinetics of the phase transitions in annealing of the titanium alloy samples subjected to

electrolytic hydrogen saturation. During linear heating at a rate of 6 °C/min, the reflections of titanium hydride begin to decrease at a temperature of 320°C and fully disappear at 370°C. However, hydrogen desorption begins at a temperature of 550°C (Fig. 4). These results demonstrate that hydrogen atoms dissolve in the titanium lattice after dissociation. The hydride dissociation temperature (320°C) corresponds to the boundary between the $\alpha + \delta$ and $\alpha + \beta$ phase fields in the phase diagram [12]. Thus, the hydrogen electrolytic saturation of the titanium alloy results in the formation of a surface layer consisting of δ hydrides in the alloys samples.

Figure 8 shows the X-ray diffraction patterns that demonstrate the kinetics of the phase transitions in heating in the titanium alloy samples hydrogen saturated from a gas atmosphere.

During linear heating at a rate of 6 °C/min, the reflections of titanium hydride begin to decrease at a



temperature of 520°C and fully disappear at 530°C, and hydrogen desorption begins (Fig. 5). However, hydrogen desorption begins at a temperature of 550°C (Fig. 5). The hydride dissociation temperature (530°C) corresponds to the boundary between the δ and $\beta + \delta$ phase fields in the phase diagram [12]. Thus, the hydrogen saturation of the titanium alloy from a gas atmosphere results in the formation of δ hydrides throughout the alloy volume.

A further increase in the temperature from 530°C is accompanied by a decrease in the reflection intensities of α -titanium and by an increase in the reflection intensities of β -titanium, which indicates gradual transformation of titanium from the α into the β modification. At a temperature of 690–720°C, α -titanium fully transforms into β -titanium, and another peak appears in a thermally stimulated hydrogen desorption spectrum (Fig. 5).

CONCLUSIONS

We experimentally detected that the electrolytic hydrogen saturation of a VT1-0 titanium alloy in an M-solution of sulfuric acid at an electric current of 0.73 A and an electrolyte temperature of 70°C for 360 min results in the formation of a 0.4- μ m-thick surface layer consisting of δ hydrides with a binding energy of 108 kJ/mol. The dissociation of the electrolytically formed hydrides in heating occurs in the temperature range 320–370°C. The hydrogen saturation from a gas atmosphere at a temperature of 600°C for 60 min and a hydrogen pressure of 6.6×10^4 Pa in a chamber results in the formation of δ hydrides with a binding energy of 102 kJ/mol throughout the sample volume. The dissociation of the hydrides formed during gas-phase saturation in heating occurs in the temperature range 520–530°C. A further increase in the temperature is accompanied by the transformation of titanium from the α into the β modification. At 690–720°C, α -titanium almost fully transformed into β -titanium, and another hydrogen desorption peak appears in a thermally stimulated hydrogen desorption spectrum.

ACKNOWLEDGMENTS

I am grateful to A.N. Shmakov for his assistance with this study at the Precision X-ray Diffraction II

Station, Institute of Catalysis, Siberian Branch, Russian Academy of Sciences.

REFERENCES

1. K. Wang, *Mater. Sci. Eng., A* **213**, 134 (1996).
2. I. Gurrappa, *Mater. Characterization* **51**, 131 (2003).
3. R. W. Schutz and H. B. Watkins, *Mater. Sci. Eng., A* **243**, 305 (1998).
4. M. Yamada, *Mater. Sci. Eng., A* **213**, 8 (1996).
5. W. D. Brewer, R. K. Bird, and T. A. Wallace, *Mater. Sci. Eng., A* **243**, 299 (1998).
6. V. Madina and I. Azkarate, *Int. J. Hydrog. Energy* **34**, 5976 (2009).
7. E. Lunarska, O. Chernyayeva, D. Lisovytskiy, et al., *Mater. Sci. Eng., C* **30**, 181 (2010).
8. Y. Furuya, A. Takasaki, K. Mizuno, et al., *J. Alloys Compd.* **446–447**, 447 (2007).
9. D. Eliezer, E. Tal-Gutelmacher, C. E. Cross, et al., *Mater. Sci. Eng. A* **421**, 200 (2006).
10. E. Tal-Gutelmacher, D. Eliezer, and E. Abramov, *Mater. Sci. Eng. A* **445–446**, 625 (2007).
11. F. Zeppelin, M. Haluska, and M. Hirscher, *Thermochim. Acta* **404**, 251 (2003).
12. A. Takasaki, Y. Furuya, K. Ojima, et al., *J. Alloys Compd.* **224**, 269 (1995).
13. L. V. Gulidova, V. N. Kudiyarov, N. A. Dubrova, and A. M. Lider, *Al'tern. Energ. Ekol.*, No. 03/2 (122), 32 (2013).
14. A. M. Lider, N. S. Pushilina, V. N. Kudiyarov, et al., *Appl. Mech. Mater.* **302**, 92 (2013).
15. S. M. Lee and J. Y. L. Lee, *Appl. Phys.* **63**, 4758 (1988).
16. A. N. Shmakov, B. P. Tolochko, I. L. Zhogin, and M. A. Sheromov, "X-ray synchrotron radiation, neutrons and electrons for investigation of nanosystems and materials," in *Proceeding of the 7th National Conference on Nano-Bio-Info-Cognitive Technologies, RSNE-NBIK, IKRAN-RNTsKI, Moscow, 16–21 November, 2009*, p. 559.
17. A. N. Shmakov, M. G. Ivanov, B. P. Tolochko, M. R. Sharafutdinov, A. I. Ancharov, I. L. Zhogin, and M. A. Sheromov, in *Proceedings of the 18th International Conference on the Applications of Synchrotron Radiation, Novosibirsk, 2010*, p. 68.
18. V. M. Aul'chenko, *Proceedings of the School of Young Specialists on Synchrotron Radiation: Diffraction and Scattering, Novosibirsk, 2009*, pp. 6–9.
19. L. Yan, S. Ramamurthy, J. J. Noel, et al., *Electrochim. Acta* **52**, 1169 (2006).