

Investigation of Hydrogenation Parameters Influence on the Hydrogen Sorption Rate by Titanium with Nickel Layer

Viktor Kudiiarov^{a)}, Maxim Syrtanov^{b)}, Egor Kashkarov^{c)}, Maria Babikhina^{d)}

Tomsk Polytechnic University, 30 Lenina Avenue, Tomsk 634050 Russian Federation

^{a)}victor31479@mail.ru

^{b)} corresponding author: maxim-syrtanov@mail.ru

^{c)}egor_kashkarov@mail.ru

^{d)}m.babihina@mail.ru

Abstract. The influence of hydrogenation parameters on the hydrogen sorption rate by commercially pure titanium alloy coated by nickel layer was investigated. Sievert apparatus was used for investigation of hydrogen interaction with commercially pure titanium alloy. It was shown that increasing the coating deposition time from 10 to 50 minutes reduces the hydrogen sorption rate more than 7 times. With increasing temperature from 350 °C to 550 °C the hydrogen sorption rate increases more than 20 times in the pressure range of 1-2 atm. Increasing the hydrogen pressure in the chamber from 1 to 2 atm. accelerates the hydrogenation process by several times. The activation energy of hydrogen adsorption increases with hydrogenation pressure.

INTRODUCTION

Titanium and titanium-based alloys are widely used in medicine, gas, oil and aerospace industries as construction materials due to their high mechanical properties [1, 2]. Hydrogen interaction with such materials is actual problem studied for many years. The penetration and accumulation of hydrogen in titanium structural components lead to degradation of physical, mechanical and operational properties caused by hydrogen embrittlement and delayed hydride cracking [3, 4].

Hydrogen interaction with metals includes following processes: adsorption, absorption and diffusion of hydrogen in the bulk of the material. The main role of each process changes under different hydrogenation conditions. For example, gradient depth distribution of hydrogen can be obtained when the bulk diffusion is much slower than the process of hydrogen absorption, or uniform distribution when the rate of bulk diffusion is equal or greater than hydrogen absorption by the surface [5]. Another important factor influenced the adsorption process is the state of surface, especially for easily oxidized materials. For example, different surface modification and coating deposition methods are used to prevent hydrogen penetration [6-10]. However, to investigate the mechanism of hydrogen interaction and sorption kinetics of titanium alloys it is necessary to simulate different hydrogen penetration conditions, in particular to control hydrogen absorption rate. Thus, it is also necessary to investigate high rate hydrogen sorption by titanium alloys that can be achieved by deposition of thin nickel layer on the metal surface. Nickel has a high physical adsorption of hydrogen and permeability that increases hydrogen sorption rate. Furthermore, the oxidation rate of nickel is significantly lower than that for titanium alloy which promotes hydrogen adsorption [11-13]. On the other hand, hydrogen sorption rate depends on the hydrogenation parameters. The main hydrogenation parameters are temperature and pressure in the reaction chamber [3, 14-17].

Thus, the aim of this work is to study the influence of hydrogenation parameters on the kinetics of hydrogen sorption by commercially pure titanium alloy with nickel layer deposited by magnetron sputtering.

MATERIAL AND METHODS

The samples with the fixed size of 20×20×1 mm were cut from commercially pure titanium alloy and used as a substrate material. Initially, the samples were polished to the average roughness R_a of 0.05 μm to remove oxides and organic contamination from the surface. After polishing, the samples were subjected to argon ions bombardment at 1500 V and 0.3 A for 5 min. Finally, nickel was deposited by magnetron sputtering using “Raduga Spekr” equipment.

Hydrogenation of the samples was performed from gas atmosphere using Gas Reaction Controller LPB (USA). The chamber was evacuated and heated to 350, 450 or 550 °C with the heating rate of 6 °C/min. After heating, the chamber was filled with hydrogen. They were kept in a hydrogen atmosphere at constant pressure of 1, 1.5 and 2 atm for 1 hour and slowly (at the rate of 2 °C/min) cooled.

The calculation of adsorption activation energy consists of two stages: calculation of hydrogen absorption rate q in the initial region of hydrogenation; linear approximation of the relation between natural logarithm of hydrogen sorption rate $\ln q$ and inverse temperature $1000/T$. The resulting value of adsorption activation energy determines by the relation [18]:

$$E_a = -R \frac{\Delta \ln q}{\Delta(1000/T)} \quad (1)$$

where R – gas constant (8.314 Jmol⁻¹K⁻¹), q – hydrogen absorption rate (wt.%/sec) and T – temperature (K).

RESULTS AND DISCUSSION

Nickel coatings were deposited on titanium alloy by magnetron sputtering for 10-50 minutes to study the material sorption properties. Discharge power and argon pressure in the chamber were 2.2 kW and 0.12 Pa, respectively. At the next stage the samples were saturated by hydrogen from the gas phase at a temperature of 450 °C. for 1 hour. The pressure in the chamber was 2 atm. Figure 1 shows hydrogen sorption curves at different deposition time of the nickel layer.

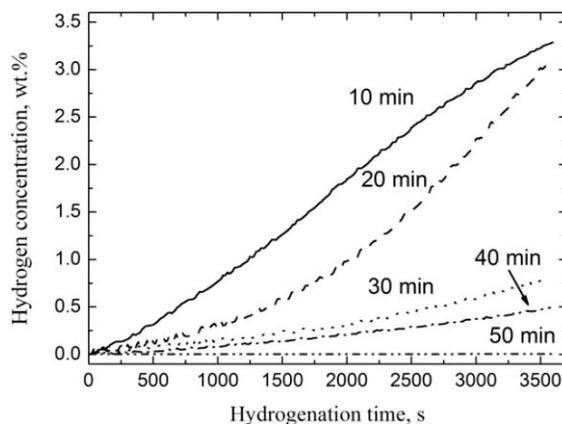


FIGURE 1. Hydrogen sorption curves of titanium alloy VT1-0 at a temperature of 450 °C and a pressure of 2 atm. with different coating deposition time

The highest hydrogen sorption rate is observed for samples with 10 and 20-minutes deposition of nickel. For the remaining samples, increasing deposition time leads to decreasing the sorption rate due to peeling of the coating. Evaluation of hydrogen sorption rate was performed on linear region of hydrogen sorption curves as slopes of curves (Figure 1). Sorption rate calculation results are shown in Table 1.

TABLE 1. Sorption rate calculation results of commercially pure titanium alloy with nickel layer at a temperature 450 °C and a pressure 2 atm.

No	Deposition time, min	Sorption rate, 10 ⁻⁴ mass.%/s
1	10	9.90
2	20	8.54
3	30	3.49
4	40	2.12
5	50	1.36

Depending on the nickel coating deposition time changes hydrogen sorption rate of titanium alloy. In this case the hydrogen sorption rate reduced more than 7 times with increasing deposition time of 10 to 50 minutes. Reducing the hydrogen sorption rate could be associated with changes in structure and morphology of the nickel layer as well as the formation of defect structure in the coating that prevents the diffusion of hydrogen deep into the material.

Samples hydrogenation was conducted at temperatures of 350 °C, 450 °C, 550 °C and hydrogen pressures in the chamber of 1 atm., 1.5 atm., 2 atm. Hydrogen sorption curves shown in Figure 2. For all samples at different hydrogenation pressures are observed a significant increase in intensity of hydrogen accumulation with increasing hydrogenation temperature. Thus, at the hydrogenation temperature of 350 °C the hydrogen content in the sample was 0.25 wt.%, while at 450 °C was 3.25 wt.%. Furthermore, it should be noted that the maximum possible concentration of hydrogen in the titanium alloy is 4.04 wt. %, which corresponds to the stoichiometric titanium hydride TiH_2 . Upon reaching the limit of the hydrogen concentration in the titanium alloy at a specified temperature the sorption curves reach saturation. Increasing the hydrogen pressure in the chamber increases the hydrogen absorption rate for the entire temperature range. The time to reach limit of the hydrogen concentration in the titanium alloy at a temperature of 550 °C reduces from 1200 to 750 seconds with increasing hydrogen pressure in the chamber from 1 to 2 atm. respectively. Thus, with increasing hydrogenation temperature increases the hydrogen diffusion rate in the titanium alloy, while the increase in the hydrogen pressure in the chamber creates a concentration gradient that promotes more intensive hydrogen diffusion.

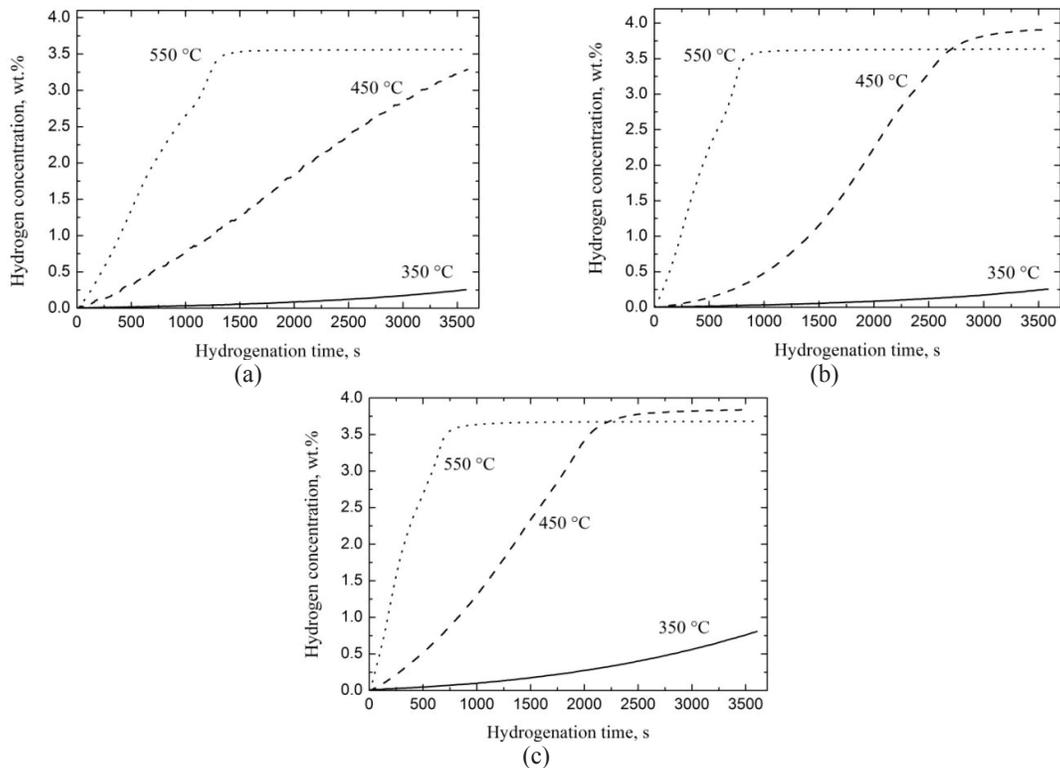


FIGURE 2. Hydrogen sorption curves of titanium alloy VT1-0 with nickel layer at temperatures of 350 °C, 450 °C, 550 °C and pressures of a) 1 atm., b) 1.5 atm., c) 2 atm.

Calculation results of the hydrogen sorption rate of technically pure titanium with nickel coating are shown in Table 2. The hydrogen sorption rate at hydrogenation temperatures of 350 °C, 450 °C and 550 °C increases by 3.4, 1.8 and 1.8 times, respectively, at change hydrogen pressure from 1 to 2 atm.

TABLE 2. Hydrogen sorption rate changes at different temperatures and pressures

No	Temperature, °C	Pressure, atm.	Sorption rate, 10^{-4} mass.%/s
1	350	1	0.65
		1.5	0.66
		2	2.2
2	450	1	9.9
		1.5	14.8
		2	17.8
3	550	1	27.1
		1.5	43.9
		2	49.2

An important stage of the hydrogenation process of the titanium alloy is a hydrogen adsorption process. The main parameter that characterizes adsorption process is the hydrogen adsorption activation energy by surface. Thus, the hydrogen adsorption activation energy was determined from the temperature dependences of the sorption rate (Fig. 3), measured at hydrogen pressures in the chamber of 1, 1.5 and 2 atm. The calculated values of the adsorption activation energy are shown in Table 3.

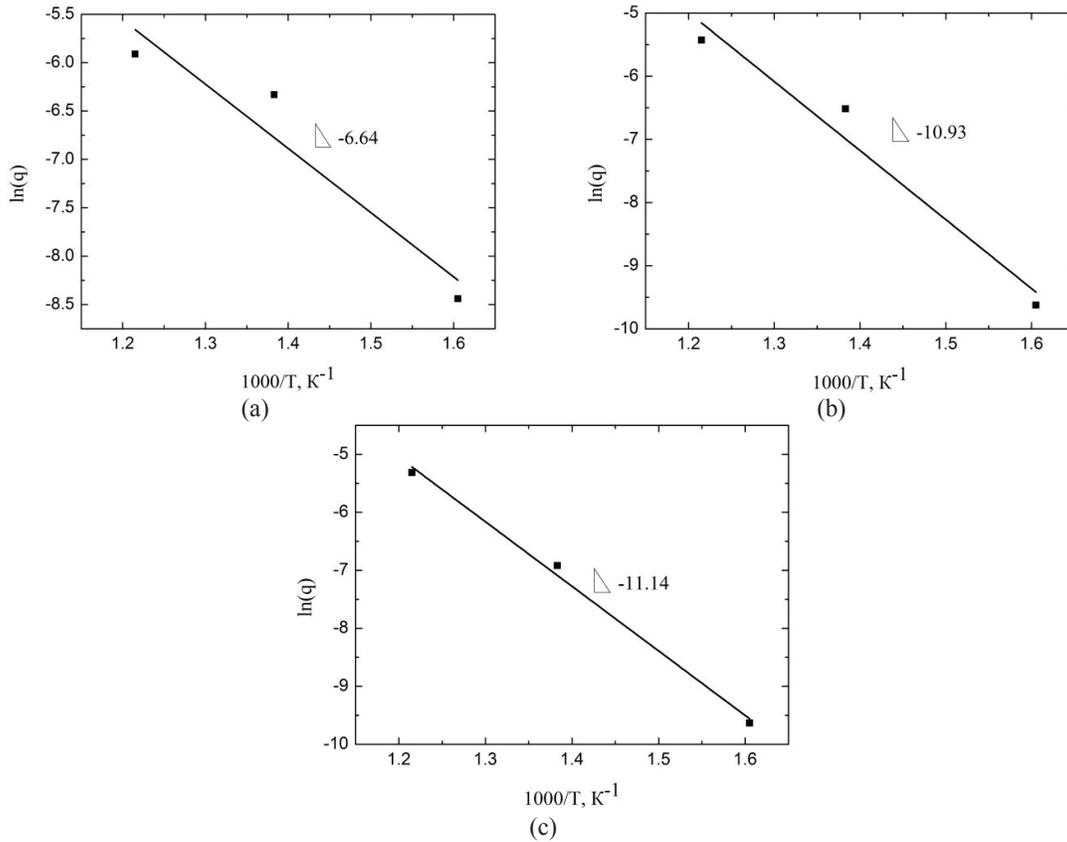


FIGURE 3. Adsorption activation energy calculation at temperatures 350 °C, 450 °C, 550 °C and pressures a) 1 atm., b) 1.5 atm, c) 2 atm.

It is found that increasing hydrogen pressure in the chamber increases the adsorption activation energy. Hydrogen adsorption activation energy of titanium alloy with the nickel coating increases by 1.7 times at increasing the hydrogen pressure in the chamber from 1 to 2 atm.

TABLE 3. The calculation results of the hydrogen adsorption activation energy by commercially pure titanium alloy with the nickel layer

№	Pressure, atm	Temperature, °C	Hydrogen adsorption activation energy, kJ/mol
1	1	350	55
		450	
		550	
2	1.5	350	90
		450	
		550	
3	2	350	92
		450	
		550	

CONCLUSION

The influence of hydrogenation parameters on hydrogen sorption rate of commercially pure titanium alloy with the nickel layer deposited by magnetron sputtering was studied. The following conclusions could be drawn from the data.

Increasing the coating deposition time from 10 to 50 minutes reduces the hydrogen sorption rate more than 7 times. However, it necessary to carry out further comprehensive studies to determine the mechanisms of hydrogen interaction with the varying thickness nickel coatings.

The hydrogen sorption kinetics of commercially pure titanium is strongly influenced on the hydrogenation parameters. The largest contribution in the adsorption rate changes makes hydrogenation temperature. The temperature increase from 350 °C to 550 °C leads to hydrogen sorption rate change more than 20 times in the pressure range of 1-2 atm. Furthermore, increasing the hydrogen pressure in the chamber from 1 to 2 atm. accelerates the hydrogenation process by several times. In this case, the hydrogen adsorption activation energy increases with the hydrogenation pressure.

ACKNOWLEDGEMENTS

This work was funded within the framework of realisation of Strategic Programme on National Research Tomsk Polytechnic University Competitiveness Enhancement in the Group of Top Level World Research and Academic Institutions.

REFERENCES

1. D. Setoyama, J. Matsunaga, H. Muta, M. Uno and S. Yamanaka, *J. Alloys Comp.* **381**(1), 215-220 (2004).
2. C. Shen and C. Wang, *J. Alloys Comp.* **601**, 274-279 (2014).
3. V. N. Kudiiarov, A. M. Lider, N. S. Pushilina and N. A. Timchenko, *Technical Physics.* **59**(9), 1378-1382 (2014).
4. O. Perevalova, A. Panin and O. Kretova, News Shidnoukraïnskogo natsionalnogo universitetu imeni Volodymyr Dahl. **9**(1), 121-125 (2013). (in Russian)
5. P. Held and R. Ryabov, *Hydrogen in metals and alloys.* (Moscow, 1974).
6. V. I. Boyko, A. N. Valyaev and A. D. Pogrebnyak, *Physics-Uspexhi.* **169**(11), 1243-1271 (1999). (in Russian)
7. E. B. Kashkarov, N. N. Nikitenkov, M. S. Syrtanov, A. N. Sutygina, I. A. Shulepov and A. M. Lider, *Appl. Surf. Sci.* **370**, 142-148 (2016).
8. N. N. Nikitenkov, A. N. Sutygina, I. A. Shulepov and E. B. Kashkarov, *Bulletin of the Russian Academy of Science: Physics.* **80**(2), 117-119 (2016).
9. N. Pushilina, V. Kudiiarov, R. Laptev, A. Lider and A. Teresov, *Surf. Coat. Techn.* **284**, 63-68 (2015).
10. N. Pushilina, V. Kudiiarov, A. Lider and A. Teresov, *J. Alloys Comp.* **645**, S476-S479 (2015).
11. S. M. Gorelov, T. E. Tsupak and E. G. Vinokurov, Specialized Exposition and Conference. 33 (2015). (in Russian)
12. T. Bibienne, V. Razafindramanana, J. Bobet and J. Huot, *J. Alloys Comp.* **620**, 101-108 (2015).
13. Kido T. and Sugano N. *Trans. At. Energy Soc. Jpn.* **1**, 469-471 (2002) (in Japanese)
14. N. S. Pushilina, A. M. Lider, V. N. Kudiiarov, I. P. Chernov and S. V. Ivanova, *J. Nucl. Mater.* **456**, 311-315 (2015).

15. R. Laptev, A. Lider, Y. Bordulev, V. Kudiyarov and G. Garanin, *J. Alloys Compd.* **645**, S193–S195 (2015).
16. Y. Bordulev, R. Laptev, V. Kudiyarov and A. Lider, *Adv. Mater. Res.* **880**, 93–100 (2014).
17. R.S. Laptev, Y.S. Bordulev, V.N. Kudiyarov, A.M. Lider and G.V. Garanin, *Adv. Mater. Res.* **880**, 134–140 (2014).
18. G. Glazunov, V. Azhazha, A. Andreev, D. Baron, M. Bondarenko, K. Kitaevskii, A. Konotopskii, I. Nekludov, A. Svinarenko and V. Stolbovoi, *Probl. Atom. Sc. Tech.* **2**, 90–94 (2009). (in Russian)