The influence of nickel layer thickness on microhardness and hydrogen sorption rate of commercially pure titanium alloy

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Abstract. The influence of nickel coating thickness on microhardness and hydrogen sorption rate by commercially pure titanium alloy was established in this work. Coating deposition was carried out by magnetron sputtering method with prior ion cleaning of surface. It was shown that increase of sputtering time from 10 to 50 minutes leads to increase coating thickness from 0.56 to 3.78 µm. It was established that increase of nickel coating thickness leads to increase of microhardness at loads less than 0.5 kg. Microhardness values for all samples are not significantly different at loads 1 kg. Hydrogen content in titanium alloy with nickel layer deposited at 10 and 20 minutes exceeds concentration in initial samples on one order of magnitude. Further increasing of deposition time of nickel coating leads to decreasing of hydrogen concentration in samples due to coating delamination in process of hydrogenation.

1. Introduction

Titanium alloys are indispensable as structural materials in aircraft, automotive, shipbuilding, nuclear, chemical and other industries [1, 2]. They have a corrosion resistance (due to the formation of the solid oxide film on the surface) and high mechanical strength. Moreover, titanium is widely spread in nature [3-7].

The mechanical properties of titanium depends on the content of impurities (H, N, O, C), which form the interstitial solid solutions with titanium and intermediate phases such as oxides, hydrides, carbides, nitrides. A content of oxygen, carbon and nitrogen increases the hardness and strength of the titanium, but reduces its plasticity. Therefore, the concentration of these impurities should not exceed 0.1 wt. %. The hydrogen content in titanium has the greatest impact on the mechanical properties. In the presence of hydrogen in titanium at the grain boundaries allocated thin brittle hydride phase plate, causing the hydrogen embrittlement. Hydrogen embrittlement leads to occurrence of internal stresses in the material. At lower temperatures, the titanium hydride becomes brittle and severe degradation of the mechanical and fracture behaviors of these alloys can occur [3]. Thus, the hydrogen content of titanium should not exceed 0.012 wt.% [3, 5].

In the process of production the hydrogen content in titanium alloys could exceed permissible value. Therefore, in the manufacture of constructions it is necessary to consider the risk of hydrogen embrittlement [7-11]. In order to study phenomenon of hydrogen embrittlement in titanium alloys require the preparation of experimental samples with different content of hydrogen for mechanical testing. However, hydrogen saturation of titanium alloys are often complicated by the presence of the surface oxide film, which significantly reduces hydrogen sorption rate, particularly at low

temperatures. To increase the sorption rate could be used ionic cleaning method for removing a surface oxide film and subsequent deposition of nickel micron-thick layer. The nickel layer significantly reduces the formation rate of the oxide film, and also actively interacts with hydrogen even at low temperatures [12]. In this paper established the influence of the nickel coating thickness on the microhardness and hydrogen sorption rate by commercially pure titanium alloy.

2. Experimental Procedure

The rectangular flat samples of commercially pure titanium alloy VT1-0 with the size of 20×20×1 mm were prepared for this experiment. The samples were mechanically polished using sandpaper and annealed in vacuum at T = 750 °C for one hour. The deposition of nickel layer on the surface of the samples was carried out by the «Raduga Spectr» technique which was developed in General Physics Department of Tomsk Polytechnic University. Samples were fixed in a vacuum chamber by the samples holder. Ultimate pressure in the chamber was equal to $2.5 \cdot 10^{-3}$ Pa. Ionic surface cleaning of the samples is of prime importance before the thin protective films sputtering. It is necessary for the removal of surface contamination of various types, as well as oxide layer removal. As a result, the ion cleaning of the surface directly before the coating process improves adhesion of the coating material with the substrate. Surface cleaning was carried out directly in the vacuum chamber before the coating deposition process by argon glow discharge at the parameters shown in Table 1.

Table 1. Parameters of the ionic surface cleaning process

Gas	Voltage, V	Power, W	Current, A	Pressure, Pa	Time, min.
Argon	1800-2000	1000	0.5	0.06	3

The nickel coating was deposited by magnetron sputtering method. High purity nickel (99,99%) was used as a target for magnetron system. Deposition parameters are presented in Table 2. Sputtering time was varied in order to form nickel layers of different thicknesses.

Table 2. Parameters of nickel magnetron sputtering

Voltage, V	Power, W	Current, A	Pressure, Pa	Time, min.
550	2000	3	0.11	10 ÷ 50

Structural and phase composition was determined by X-ray diffraction using diffractometer Shimadzu XRD 7000 (Japan). Vickers microhardness of the samples was measured using microhardness tester KB30S (Pruftechnik, Germany). The thickness of the nickel layers was determined by spherical cross-section method using Calotest CAT-S (CSEM, Switzerland). Hydrogenation was carried out from hydrogen atmosphere at 500 °C, 2 atm for 60 minutes using special equipment Gas Reaction Controller (USA) [13].

The X-ray penetration depth was varied by changing the incidence angle in an asymmetrical layout. Decreasing of the incidence angle was conducted up to complete elimination of the signal from the substrate. Evaluation of the coating thickness was carried out using the geometry of the sliding beam by the relation:

$$h = \frac{\ln(1-R)\sin\alpha \cdot \sin(2\theta - \alpha)}{\mu(\sin\alpha + \sin(2\theta - \alpha))}$$

where α –incidence angle, θ – gliding angle (Bragg angle), μ – linear absorption coefficient, R – the proportion of radiation reflected from the layer with the thickness h. When determining the thickness of the nickel coating the value of R has a value of 0.95.

3. Results and Discussion

Table 3 shows the results of nickel layer thicknesses determination by different techniques as a function of sputtering time. It has been established that the increase in sputtering time from 10 to 50 minutes increases the thickness of the nickel layer from ~ 0,56 to 3.78 μm. The results of the thickness determination by X-Ray method correlate with the results obtained by spherical cross-section method.

Non-destructive XRD analysis allows estimating the nickel layer thickness before hydrogen saturation without coating destruction.

Table 3. Results of nickel layer thicknesses determination

Time of magnetron sputtering, min	Thickness (XRD), μm	Thickness (by the method of spherical cross-section), μm
10	0.63	0.56
20	2.52	2.48
30	3.35	3.26
40	3.69	3.62
50	3.84	3.78

Figure 1 shows the dependences of Vickers microhardness on load for different samples. For the sample of titanium alloy hardness under different loads is from 140 to 170 HV. Obtained hardness values could be increased with a decrease in the indenter size [14, 15].

It is seen that at a 1 kg hardness load of all commercially pure titanium samples is approximately the same in view of the error. The hardness of the samples increases under low loads after the deposition of the nickel layer. The obtained hardness values increased with increasing coating thickness and reduced to a titanium alloy hardness values with increasing applied load. For a sample of nickel, hardness is from 200 to 210 HV in the investigated range of loads. Thus, the titanium alloy substrate has no effect on coating thickness over 3.3 μm when measuring the hardness of the samples at a load of 0.1 kg. The maximum hardness 240-260 HV observed for samples with coating thickness of 3.62 and 3.78 μm.
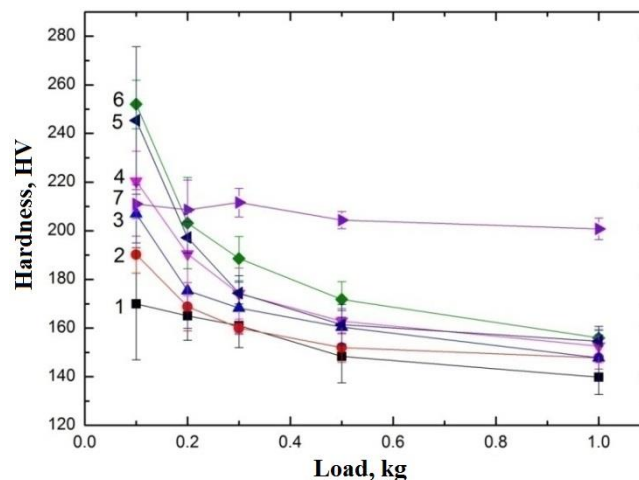

Figure 1. The dependences of Vickers microhardness on load for 1 - initial samples and for samples with different thicknesses of nickel layer: 2 - 0.56 μm; 3 - 2.48 μm; 4 - 3.26 μm; 5 - 3.62 μm; 6 - 3.78 μm and for 7 - nickel sample

Figure 2 shows the absorption curves for all samples (a) and the dependence of the hydrogen content on the deposition time of nickel (b). Comparing sorption curves is possible to say that the greatest hydrogen sorption rate   is observed in samples with 10 and 20-minutes deposition of nickel. However, the graphs have a different nature: for a sample with a 10-minutes deposition the curve is close to linear form, for the sample with 20-minutes deposition the linear dependence is observed on two linear sections from 0 to 02 wt.% and from 1.5 wt.% up to 3.25 wt.%. Between these sections which are corresponding to different phases of titanium-hydrogen system observed the break related with increasing the hydrogen sorption rate. For the remaining samples, increasing deposition time leads to decreasing the sorption rate due to peeling of the coating. Figure 2b shows that during the same saturation time the samples accumulated different hydrogen concentration. The lowest concentration is in the initial sample. The greatest, as already mentioned, for the samples with 10- and

20-minutes deposition of nickel. For the remaining samples, the hydrogen concentration is inversely proportional to the time of deposition.
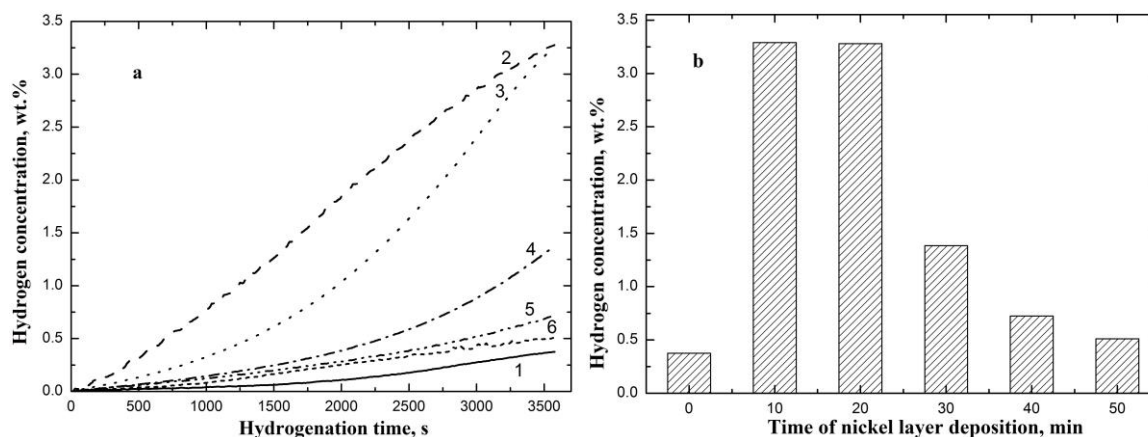

Figure 2. Hydrogen sorption curves (a) by titanium alloy with nickel layer after different time of magnetron sputtering: 1 - without nickel layer; 2 - 10 minutes; 3 - 20 minutes; 4 - 30 minutes; 5 - 40 minutes; 6 - 50 minutes, and hydrogen concentration (b) in titanium alloy with nickel layer after different time of magnetron sputtering hydrogenated at 500 °C, 2 atm, for 60 minutes

4. Conclusion

The influence of nickel layer thickness on microhardness and hydrogen sorption rate by commercially pure titanium alloy was established. Nickel coatings were deposited by the method of magnetron sputtering with ionic surface cleaning before deposition. It was showed that with deposition time increasing from 10 to 50 minutes the thickness of coatings increase from 0.56 μm to 3.62 μm. Microhardness values for all samples are not significantly different at loads 1 kg. Hydrogen content in titanium alloy with nickel layer deposited at 10 and 20 minutes exceeds concentration in initial samples on one order of magnitude. Further increasing of deposition time of nickel coating leads to decreasing of hydrogen concentration in samples due to coating delamination in process of hydrogenation.

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