

The investigation of hydrogenation influence on structure changes of zirconium with nickel layer

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Abstract. The results of experimental investigation of hydrogenation influence on structure changes of zirconium alloy (Zr-1%Nb) with thin nickel layer have presented in this work. Nickel layer was formed by magnetron sputter deposition. Hydrogenation was carried out at gas atmosphere at constant temperature. Different hydrogen concentrations were obtained by varying time of hydrogenation. Defect and phase structure was studied by means of X-ray diffraction, glow discharge optical emission spectroscopy, positron lifetime and Doppler broadening spectroscopies. New experimental data about the evolution of the positron annihilation parameters depending on hydrogen concentration in Zr-1Nb alloy with nickel layer was obtained.

1. Introduction

Penetration and accumulation of hydrogen in metal structure has a significant impact on the physical, chemical and mechanical properties of its structure. This problem is particularly topical for zirconium alloys [1-6]. The preparation process of samples with different concentrations of hydrogen and different distribution of hydrogen by volume is an essential part of metal-hydrogen systems experimental studies. It is important to bear in mind that samples are covered with an oxide film, which degrades the process of hydrogen penetration during planning the process of saturation with hydrogen of zirconium alloys.

Increase in the rate of hydrogen sorption is possible by coating the Zr surface with a layer of nickel. Nickel has a high physical and chemical adsorption activity with hydrogen and has a high permeability to hydrogen. Furthermore, the oxide film formed worse on the nickel surface than on the titanium or zirconium surfaces, which promotes to hydrogen absorption. The study of the effect of nickel layer coating on the hydrogen sorption by Zr-1%Nb alloy, and the effect of hydrogenation on the defect structure of zirconium alloy with the nickel layer is carried out in this work.

2. Experimental Procedure

Flat samples of Zr-1%Nb alloy (20×20×0.7 mm) were prepared for this experiment. Samples were mechanically polished and annealed in vacuum ($T = 580\text{ °C}$) for three hours. 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. Ionic surface cleaning method produces virtually atomically clean surface. 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 process by argon ion beam, with 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 technique with the parameters, presented in Table 2. Sputtering time was varied in order to form nickel layers of different thicknesses. High purity nickel (99,99%) was used as a target for magnetron system.

Table 2. Parameters of nickel magnetron sputtering

Voltage, V	Power, W	Current, A	Pressure, Pa	Time, min.
550	2000	3	0.11	10 ÷ 30

Structural and phase composition was determined by X-ray diffraction using diffractometer Shimadzu XRD 7000 (Japan). Hydrogenation was carried out using special equipment Gas Reaction Controller (USA) [7]. Study of the elemental composition of samples was measured by optical spectroscopy of high-frequency glow discharge performed with Profiler-2 (Horiba, Japan) [8].

The penetration depth of the X-ray beam was varied by changing the angle of incidence while the asymmetric scan by XRD. Decreasing of the angle of incidence 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:

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

where α – angle of incidence, 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.

Thicknesses of the nickel layers were additionally determined by analysing the distribution profile of elements on the depth of the samples.

3. Results and Discussion

Figure 1 shows the distribution profiles of elements in samples of zirconium alloy before (a) and after (b) nickel layer deposition. The surface layer of the initial samples ($\sim 0.3 \mu\text{m}$) consists of the oxides and contaminant gases (nitrogen and hydrogen) from the air.

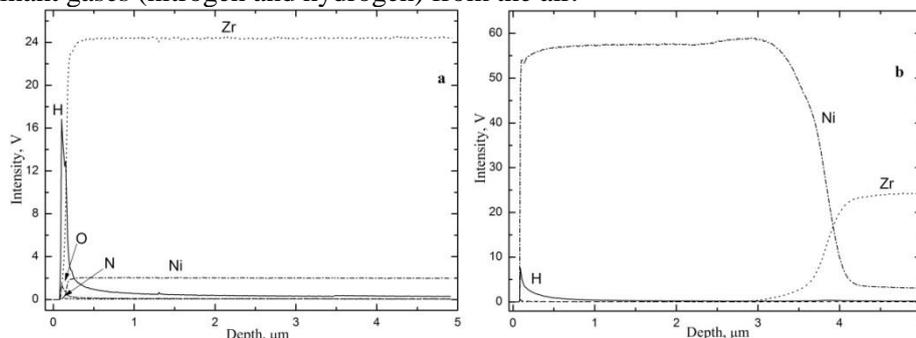


Figure 1. Distribution profiles of the elements in the Zr-1%Nb (a) and Zr-1%Nb with nickel layer (b)

Thus, the initial samples contain hydrogen only in the surface layer. Its concentration is about 0.001 weight %. The nickel layer is formed on the surface of the samples after 30 minutes of magnetron sputtering. The thickness of this layer can be determined from the distribution profile of the

elements as a depth at which the intensity of the nickel signal begins rapidly decrease and zirconium signal starts increasing.

Table 3. Results of nickel layer thicknesses determination

Time of magnetron sputtering, min	Thickness (XRD), μm	Thickness (depth profile distribution analysis), μm
10	1.2	1 ± 0.1
20	1.9	1.8 ± 0.1
30	2.6	2.7 ± 0.1

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 30 minutes increases the thickness of the nickel layer from ~ 1 to $2.7 \mu\text{m}$. The results of the thickness determination by X-Ray method correlate with the results obtained by depth profile distribution analysis. Non-destructive XRD analysis allows estimating the nickel layer thickness before hydrogen saturation.

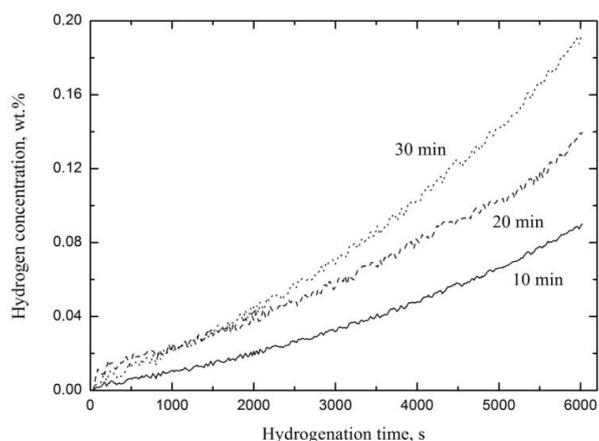


Figure 2. Hydrogen sorption curves by zirconium alloys with nickel layer of different thicknesses

Figure 2 shows that increasing of the nickel layer thickness leads to an increase in the hydrogen sorption rate of zirconium alloy.

Table 4 shows the results of defect structure studies of zirconium alloy with a layer of nickel before and after hydrogenation by positron lifetime and Doppler broadening techniques.

Table 4. Results of the defect structure studies of zirconium alloy with a layer of nickel before and after hydrogenation

Sample	Sputtering Time, min	Hydrogenation Temperature, $^{\circ}\text{C}$	Hydrogen Concentration, wt.%	τ_1 , ps	τ_2 , ps	I_2 , %	τ_{avg} , ps	Fit
Zr	-	-	-	164 ± 1	-	-	164 ± 1	1.09
Zr + Ni	10	-	-	165 ± 1	-	-	165 ± 1	1.08
Zr + Ni	10	-	-	165 ± 1	-	-	165 ± 1	1.10
Zr + Ni	20	-	-	166 ± 1	-	-	166 ± 1	1.10
Zr + Ni	30	-	-	167 ± 1	-	-	167 ± 1	1.09
Zr + Ni	10	550	2.1	164 ± 1	183 ± 2	53.5 ± 2	176 ± 1	1.12
Zr + Ni	10	450	2.1	164 ± 1	183 ± 2	65.1 ± 2	178 ± 1	1.10
Zr + Ni	10	300	0.15	164 ± 1	183 ± 2	84.5 ± 5	182 ± 1	1.10
Zr + Ni	20	300	0.15	164 ± 1	209 ± 3	10 ± 2	169 ± 1	1.12
Zr + Ni	30	300	0.15	164 ± 1	241 ± 5	7.8 ± 1	170 ± 1	1.07

The positron lifetime in the annealed zirconium alloy is 164 ± 1 ps, which is consistent with a lifetime of positrons zirconium lattice [9], and after coating the lifetime of this component increases slightly. There are no any other components in the positron lifetime spectra. This is apparently due to the use of ^{44}Ti radioisotope as a source of positrons. Since the maximum energy of positrons from this source is 1.47 MeV, information is collected from the volume of material. Using the method proposed in [10], as well as LYS-1 software [11], positron implantation profile in the sample of Zr-1%Nb with a layer of nickel was calculated (Figure 3). The figure shows that more than 95% of the positrons annihilate in the volume of the Zr-1%Nb.

Hydrogenation has a significant impact on the lifetime distribution of positrons in the material. The intensive component (50-85 %) with a lifetime of 183 ± 2 ps is appeared in the samples with the high hydrogen concentration. This positron lifetime corresponds to positron lifetime in a zirconium ZrH_2 [12].

The long-lived component of positron lifetime with a lifetime values of 209 ± 3 ps and 239 ± 5 ps appears in a spectra for the samples with low hydrogen concentrations. The positron lifetime value of 241 ± 5 ps corresponds to the lifetime of positron, trapped in single vacancy [9]. The lifetime of 209 ± 3 ps is significantly higher than the lifetime of positrons, trapped at dislocations (197 ps), but lower than the lifetime in a single vacancy. Apparently, this component corresponds to the positron lifetime in a hydrogen-vacancy defects (mV-nH), formed in the process of hydrogen saturation [6, 7].

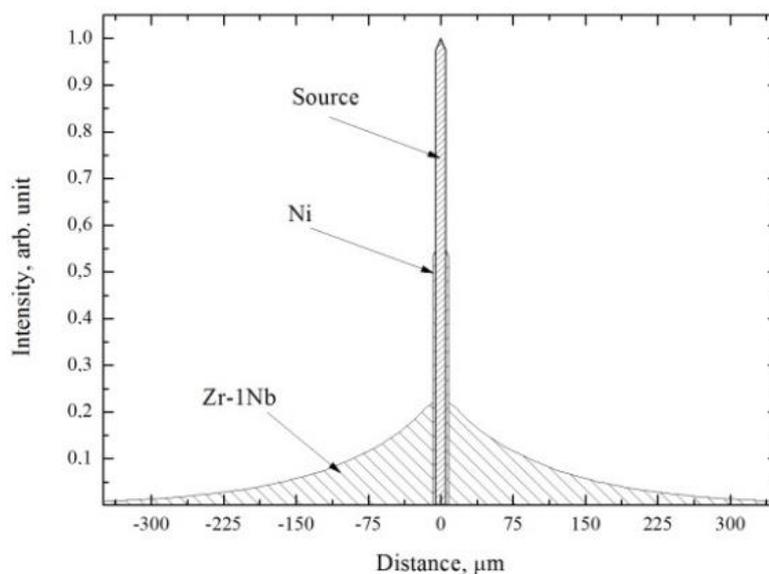


Figure 3. Positron implantation profile in a Zr1%Nb alloy with a layer of Ni for ^{44}Ti positron source

Analysis of Doppler broadening spectra (DBS) confirms these assumptions. The values of the line-shape parameters (S- and W- parameters) of DBS for the samples with nickel layer are virtually identical to the values of these parameters for the initial sample. The relative deviation is less than 1%. Figure 4 shows the dependence of the relative parameters S/S_0 and W/W_0 on the hydrogen content.

The graph shows that at low concentrations of hydrogenation the decrease of the relative parameters S/S_0 and growth of W/W_0 are observed. It also may indicate the formation of hydrogen-vacancy complexes [13-15].

The relative growth of S/S_0 and W/W_0 parameters is observed in the samples saturated up to high concentrations of 1.2 and 2.1 wt.% at the temperatures of 350 °C and 450 °C respectively. It can be possible due to the formation of hydrides, as well as changes in the microstructure, connected with hydride phase formation. In addition to the above, for the samples, that have been saturated up to 2.1 wt.% at 550 °C, S/S_0 parameter increases and W/W_0 parameter is decreases. This is the evidence of the vacancy-type defects formation [16].

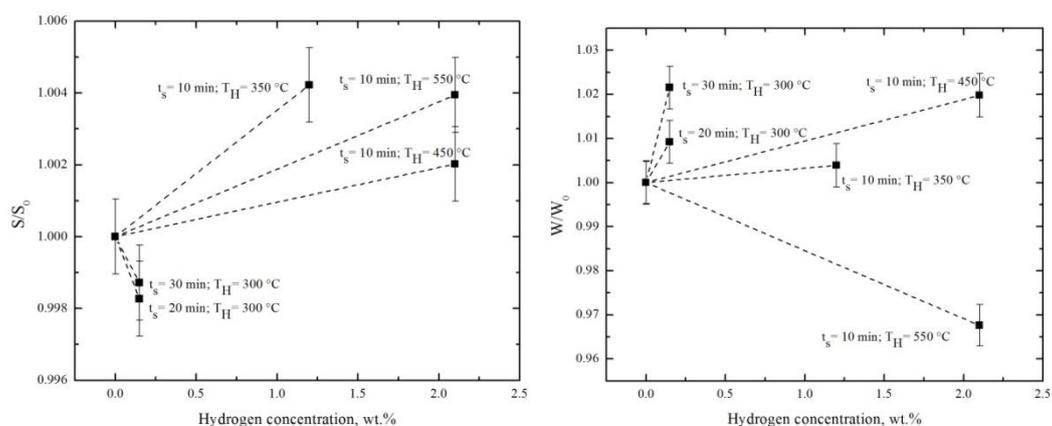


Figure 4. Dependence of S/S_0 parameter (a) and W/W_0 parameter (b) on the hydrogen content. t_s – time of Ni layer sputtering, T_H – temperature of hydrogen saturation

4. Conclusion

Magnetron sputtered nickel layer with different thickness from 1 to 3.4 μm was deposited. It was shown that increasing of the nickel layer thickness leads to an increase in the hydrogen sorption rate of zirconium alloy. The positron lifetime in the annealed zirconium is equal to lifetime of positrons zirconium lattice. Hydrogenation has a significant impact on the lifetime distribution of positrons in the material. The long-lived component of positron lifetime corresponds to the lifetime of positron, trapped in single vacancy appears in a spectra for the samples with low hydrogen concentrations. The intensive component correspond to positron lifetime in a zirconium hydride is appeared in the samples with the high hydrogen concentration.

Acknowledgements

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

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