

Influence of Surface State on Hydrogen Sorption by Zirconium Alloy Zr1Nb

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Abstract. This work is focused on the investigation of hydrogen sorption behavior by zirconium alloy Zr1Nb with different surface states. Zirconium alloy samples in initial state, after ion cleaning with subsequent nickel deposition and after treatment by Low Energy High Current Pulsed Electron Beam (LEHCPEB) were hydrogenated at constant pressure and different temperatures. Hydrogen sorption rates as well as the energy of hydrogen adsorption by zirconium alloy with different surface states have been evaluated. It was shown, that ion cleaning with subsequent nickel deposition leads to the hydrogen sorption rate increasing at temperatures 350 – 550 °C, while the energy of hydrogen adsorption by zirconium alloy reduces on 15%. Modification by LEHCPEB leads to the hydrogen sorption rate decreasing at temperatures 350 – 550 °C, while the energy of hydrogen adsorption by zirconium alloy grows on 15%.

INTRODUCTION

Zirconium alloys are used in nuclear reactors as soon as they have low cross-section of thermal neutron capture, corrosion resistance, good strength characteristics and resistance to radiation damage. Fuel claddings, spacer grids, guide tubes are made from zirconium alloys in reactors. Low hydrogen uptake is important requirement for zirconium claddings due to the fact that hydrogen in zirconium can cause embrittlement and destruction. Hydrogen solubility in zirconium at room temperature is equal $1 \cdot 10^{-5}$ wt.%, at exploitation temperature (~ 320 °C) this value is $2 \cdot 10^{-2}$ wt.%. Hydride phases are formed in zirconium after hydrogen exceeding the value of solubility. Hydrides have lower ductility compared to zirconium and can serve as areas of cracks formation with a further crack opening, including in zirconium matrix [1-4].

The level of zirconium alloys hydrogenation essentially depends on the surface state and on the operating conditions. The main factor that determines hydrogen behavior with zirconium alloys is oxide film on the material surface. Zirconium alloys weakly absorbs hydrogen even at high temperatures in the presence of thin oxide film on the surface. On the one hand the presence of this film plays a positive role in the operation conditions, as this reduces the hydrogen permeability. On the other hand, there is a need to prepare experimental samples of zirconium alloys with different hydrogen concentrations and distribution for further studies (for example, for mechanical testing). In the preparation of the experimental samples the presence of oxide film will prevent the hydrogenation, and in some cases, when the hydrogenation temperature is limited (for example, there has been a pre-heat treatment of the material), making it impossible. Therefore, it becomes necessary to investigate ways to reduce and to increase the hydrogen permeability [5-8].

Ion cleaning with subsequent nickel deposition can be used for hydrogen permeation increasing of zirconium alloys. Ion cleaning removes oxide film from metal and nickel deposition right after cleaning protects surface from oxidation. Moreover, nickel is an alloying element that promotes hydrogen absorption due to the suppression of hydrogen atoms recombination in the molecule [9-10]. Surface modification by Low Energy High Current Pulsed Electron Beam (LEHCPEB) is advance method for hydrogen permeation decreasing. This effect is caused by quenching structure formation in surface layer after irradiation and thin oxide film formation [11-14]. This work is focused on the investigation of surface state (initial state, after ion cleaning with

subsequent nickel deposition, modification by pulsed electron beam) influence on the hydrogen behavior of zirconium alloy Zr1Nb.

MATERIAL AND EXPERIMENTAL METHODS

Samples of zirconium alloy Zr1Nb with dimensions 20×20×0.7 were used for research. Samples were grinded and polished. Part of samples was cleaned by Ar ions with subsequent nickel layer deposition by magnetron sputtering method with the help of “Raduga-Spektr” equipment (Russia). 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

Other part of samples was irradiated by LEHCPEB on the “SOLO” equipment. “SOLO” equipment allows to generate electron beam with diameter up to 30 mm with current of beam up to 300 A. The duration of pulses can be varied from 50 to 200 μ s. The both sides of each sample were treated with an energy density of 18 J/cm². Electron energy was 18 keV, every sample was irradiated by three pulses for duration of 50 μ s. Samples hydrogenation was done with the help of automated complex Gas Reaction Controller LPB at constant pressure 2 atm and different temperatures (350 – 550 °C). Hydrogen sorption rates have been calculated from hydrogen sorption curves. In additional, the values of hydrogen adsorption activation energy have been evaluated with the help of formula [15-16]:

$$\frac{d \ln(q)}{d\left(\frac{1}{T}\right)} = -\frac{E}{R} \quad (1)$$

where q is hydrogen sorption rate and T is temperature.

RESULTS AND DISCUSSION

Figure 1 shows the hydrogen sorption curves at constant pressure and different temperatures for Zr1Nb zirconium alloy in initial state (Fig.1a), after surface cleaning by ions and nickel deposition (Fig.1b) and after treatment by LEHCPEB (Fig.1c). There is linear dependence of hydrogen sorption rate from hydrogenation time before the saturation of the α -phase with hydrogen. There are changes in slope on the sorption curves that caused by the change of hydrogen diffusion rate in the material due to phase transitions. For instance, at the saturation temperature of 450 °C the sorption rate change is caused by $\alpha \rightarrow (\alpha+\delta) \rightarrow \delta$ transitions. If the hydrogenation time is increased further, the hydrogen diffusion rate is significantly decreased. These results conform well to a theory, since the hydrogen diffusion in the hydride phase is known to be two orders of magnitude lower – than the diffusion in α and β phases of zirconium. Another tendency is attributed to the fact that a zirconium hydride lattice containing more than 46.3 at. % of hydrogen at such temperatures becomes thermodynamically unstable and tends to change composition. At 550 °C the first inflexion point is observed at hydrogen concentrations of about 24.7 at. %, which matches the phase transition of $(\alpha+\delta)$ into the phase β . The next stage is a saturation of the β phase with hydrogen. During the hydrogen saturation of the LEHCPEB treated samples at the temperature range of (350 – 450) °C the hydrogen adsorption rate during the whole experiment does not change. Increasing the temperature leads to an increase in the rate of hydrogenation. At 550 °C the hydrogen diffusion rate changes is caused by the $\alpha \rightarrow (\alpha+\beta) \rightarrow (\beta+\delta) \rightarrow \delta$ phase transitions.

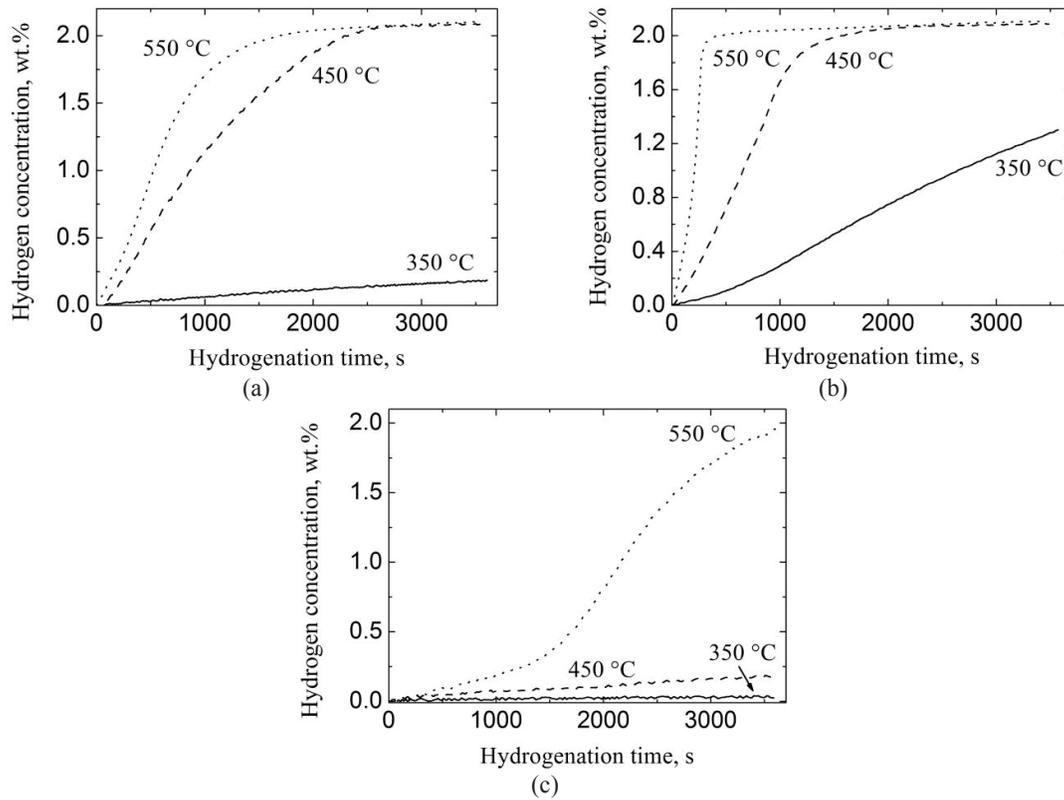


FIGURE 1. Hydrogen sorption curves by Zr1Nb (a), Zr1Nb + Ni (b) and Zr1Nb + LEHCPEB (c) at pressure 2 atm and different temperatures

The calculation results of hydrogen sorption rates by zirconium alloy with different surface states at different temperatures are shown in Table 3. Hydrogen sorption rates were calculated on the linear parts as slopes of curves. Surface modification by LEHCPEB leads to the significant decreasing of the hydrogen sorption rate compared with initial material. Surface cleaning by ions with subsequent nickel layer deposition increases hydrogen sorption rate.

TABLE 3. The results of hydrogen sorption rates determination at different temperatures of hydrogenation

T, °C	Hydrogen sorption rate, 10 ⁻⁴ wt.%/s		
	Initial state	After nickel deposition	After treatment by LEHCPEB
350	0.5	4	0.074
450	9.4	16.9	0.46
550	18.3	67.3	2.3

The dependence of $\ln(q)$ on $1/T$ for Zr1Nb zirconium alloy with different surface states are shown in Fig.2. These dependences are needed for calculation of the hydrogen adsorption activation energy. Numbers on Fig. 2 are the slopes of the straights.

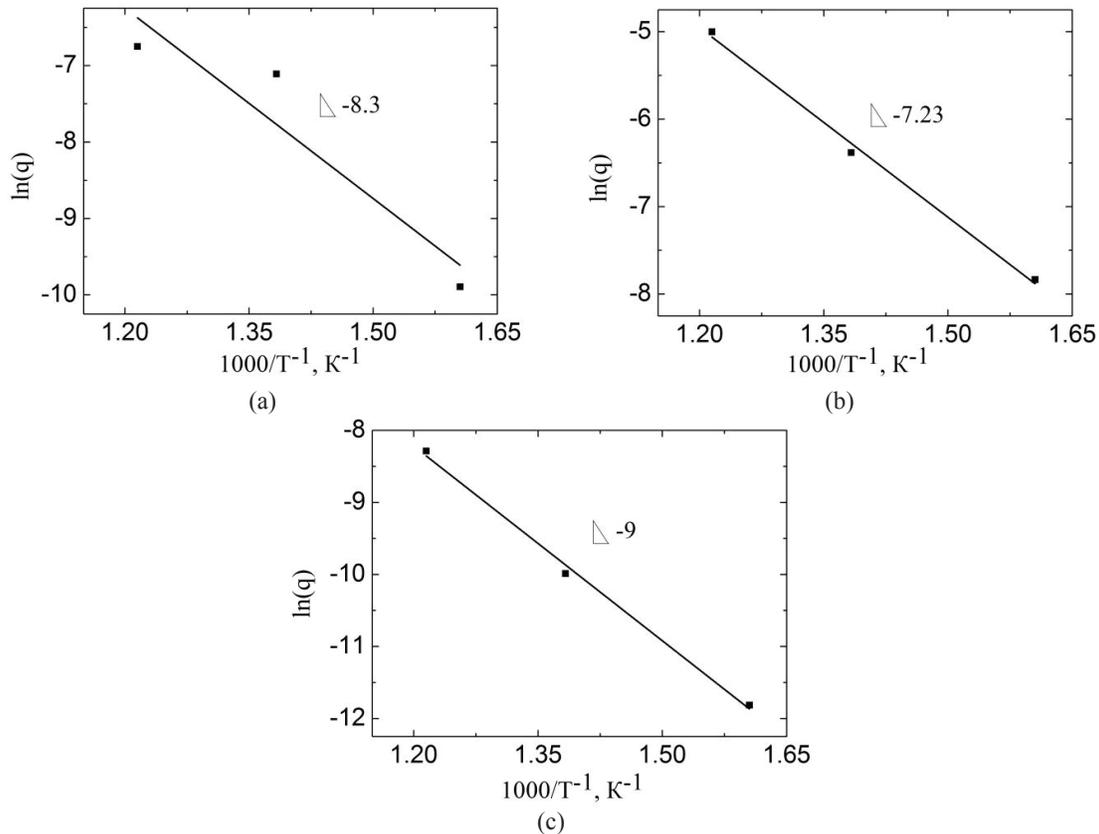


FIGURE 2. The dependence of $\ln(q)$ on $1/T$ for Zr1Nb (a), Zr1Nb + Ni (b) and Zr1Nb + LEHCPEB (c)

The hydrogen adsorption activation energies for Zr1Nb zirconium alloy in initial state, after surface cleaning with subsequent nickel layer deposition and after treatment by LEHCPEB have been calculated with the help of formula 1 and figure 2. The hydrogen adsorption activation energy for Zr1Nb zirconium alloy in initial state is equal 69 kJ/mol; for alloy after surface cleaning with subsequent nickel layer it this value is 60 kJ/mol; and for alloy after treatment by LEHCPEB the value of energy is 75 kJ/mol. The hydrogen adsorption activation energy decreasing for Zr1Nb zirconium alloy after surface cleaning with subsequent nickel layer deposition is caused by oxide layer removing. The hydrogen adsorption activation energy increasing for Zr1Nb zirconium alloy after treatment by LEHCPEB is caused by oxide layer formation.

CONCLUSION

Ion cleaning with subsequent nickel layer deposition leads to the significant hydrogen sorption rates increasing by Zr1Nb zirconium alloy at different temperatures (350 – 550 °C), and to the reducing of the value of hydrogen adsorption activation energy on 15 %. It is caused by oxide film removing from metal surface and protecting it from oxidation by nickel layer. Zirconium alloy surface modification by LEHCPEB leads to the significant hydrogen sorption rates decreasing at different temperatures (350 – 550 °C), and to the growing of the value of hydrogen adsorption activation energy on 10%. It is caused by oxide film formation on the zirconium alloy surface after irradiation.

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