

Hydrogenation of Zr–2.5Nb alloy after plasma-immersion titanium implantation

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Abstract. The study results of the influence of plasma-immersion ion implantation of titanium in Zr–2.5Nb on hydrogenation are presented. The titanium implantation was carried out in two modes: with active plasma filtering (APF) and passive plasma filtering (PPF). The results of total hydrogen concentration, absorption rate, XRD analyses and depth distribution of elements revealed that modified surface layer after titanium ion implantation is formed hydrogen diffusion barrier reduces hydrogen absorption by Zr–2.5Nb.

1. Introduction

Zirconium and its alloys are important structural materials of nuclear reactors. Zirconium is used in the nuclear reactors as the fuel assemblies cases, channels of control and protection system, the technological channels and the channel pipes.

In these reactors there is a problem of water radiolysis under the influence of radiation resulted the release of hydrogen. Zirconium alloys absorbs and accumulates hydrogen that leads to the hydrogen corrosion and embrittlement of the material. The presence of high temperatures, pressure, mechanical loads lead to the mechanical properties degradation [1-7]. All these factors reduce the operation time of zirconium elements.

One of the ways to solve these problems is the surface modification and deposition of thin surface layers (ion-plasma metal deposition, ion implantation and surface modification by pulsed ion beam) [8, 9]. One of the most perspective methods for modifying microstructure and elemental composition is plasma immersion ion implantation (PIII). PIII is the modification method of the surface by accelerated ions from the plasma arc discharge by applying a high voltage pulse current on the sample. PIII allows the ion implantation in the volume target and modify the deep layers of materials [10]. PIII leads to formation intermetallic phases and solid solutions of high concentration. As a result wear resistance, adhesive strength, corrosion resistance are increased after PIII [11]. This is due to the high concentration of implanted elements and the high target temperature reached during ion implantation [12].

Titanium implantation into steel, nickel, aluminum increases the hardness, corrosion resistance and improved tribological properties. Furthermore titanium has a low capture cross section of thermal neutrons. Titanium implantation into Zr–2.5Nb improves oxidation and corrosion behaviors [13, 14]. Therefore in this work titanium is implanted into Zr–2.5Nb. At the moment there are few studies about titanium implantation into Zr–2.5Nb and its influence on hydrogenation.

In according with this, the aim of the work is the study of the influence of titanium PIII with active plasma filter (APF) and with passive plasma filter (PPF) on hydrogenation of Zr–2.5Nb alloy.



2. Materials and Methods

Zr–2.5Nb samples with fixed size of 1 mm in thickness and 30 mm in diameter were previously polished to the average roughness R_a of 0.045 μm using sandpaper and diamond paste. The chamber was evacuated to the base pressure of lower than 2.5×10^{-3} Pa. Before deposition samples were subjected to ion bombardment in argon glow discharge at 1500 V for 3 min. For PIII – the cathode vacuum arc evaporation system equipped with coaxial plasma filter (designed by authors [15, 16]) was used. Ti (99.99 % purity) was used as the cathode material. Process parameters for PIII of Ti are: 0.15 Pa total pressure, 70 A arc current, 1500 V pulsed substrate bias with 100 kHz pulse repetition frequency and 3 A peak pulse current. The implantation time was 15 min. The part of the samples was implanted in active filtration mode (APF) another part in passive filtration mode (PPF).

Hydrogenation of the samples was performed by Sievert method (from hydrogen atmosphere) on the automated complex Gas Reaction Controller LPB (USA) during 120 min at 673 K temperature. The heating rate and hydrogen pressure in the chamber was 6 K/min and 2 atm respectively. The hydrogenation temperature was chosen due to the working temperature of zirconium fuel cladding in the operation process of nuclear reactors. Hydrogen absorption rate was measured from the absorption curves after hydrogen saturation.

The phase identification and structural investigations were performed by X-ray diffraction with $\text{CuK}\alpha$ radiation (1.5410 Å wavelength) using Shimadzu XRD-7000 (Japan) diffractometer in asymmetric mode at 40 kV, 30 mA and $\theta=3^\circ$ fixed angle. Study of the elemental composition of samples was performed by high-frequency glow discharge optical emission spectroscopy (GD-OES) with GD-Profilier 2 technique (Horiba, Japan). Hydrogen concentration was measured according to the principle of melting in inert gas at hydrogen analyzer RHEN602 (LECO, USA).

3. Results and discussion

Figure 1 shows the total hydrogen concentration in the samples volume after hydrogen saturation. The total hydrogen concentration decreases in ~ 19 times and ~ 2.2 times in comparison with the initial Zr–2.5Nb after hydrogen saturation of Ti-implanted sample with APF and PPF respectively.

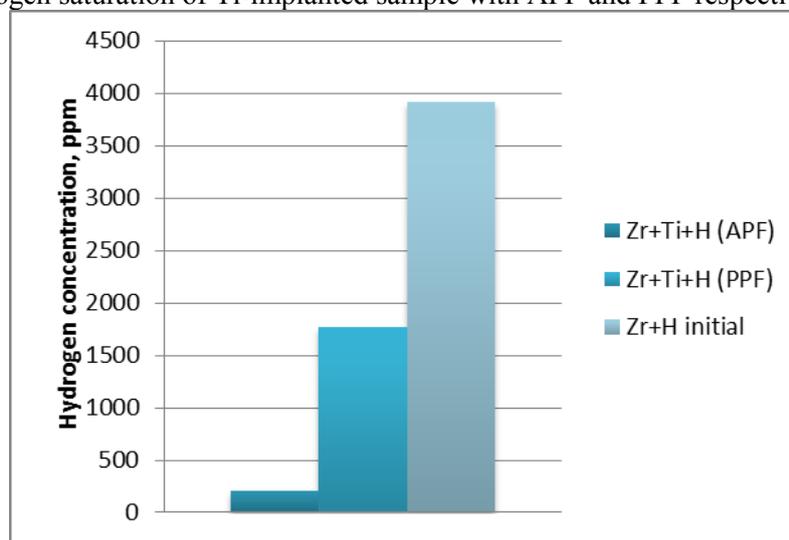


Figure 1. Hydrogen concentration of the initial and Ti implanted Zr–2.5Nb alloy after hydrogen saturation

Figure 2 shows that the average hydrogen absorption rate of Zr–2.5Nb after Ti implantation decreased from $13.65 \cdot 10^{-4}$ to $0.74 \cdot 10^{-4} \text{ cm}^3 \text{ H}_2 / (\text{sec} \cdot \text{cm}^2)$ after APF and to $3.2 \cdot 10^{-4} \cdot \text{cm}^3 \text{ H}_2 / (\text{sec} \cdot \text{cm}^2)$ after PPF.

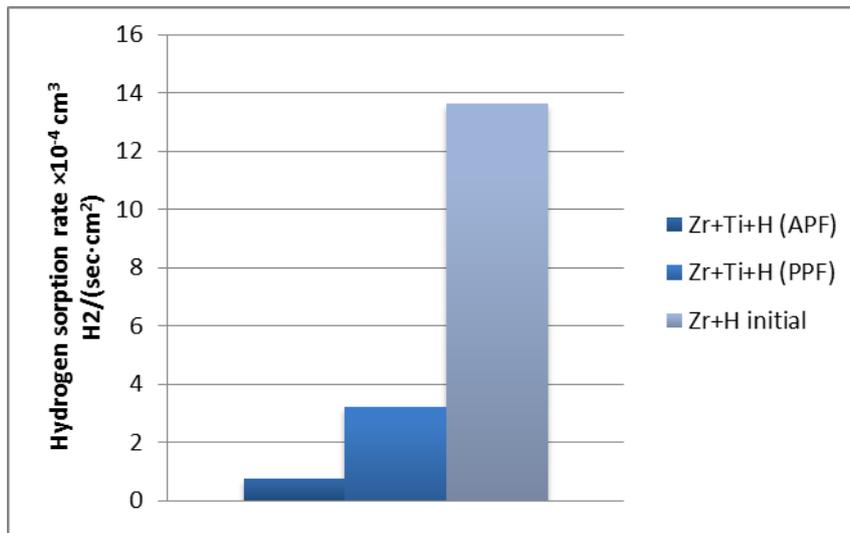


Figure 2. Average hydrogen absorption rate by Zr–2.5Nb after Ti implantation with APF and PPF modes

The hydrogen absorption rate was determined by differentiating the kinetics curve which characterized the dependence between hydrogen pressure in the chamber and time of saturation on the linear region and is calculated by the following formula:

$$q = \frac{V}{t \cdot S} \frac{P_0 - P}{P}, \quad (1)$$

where V – chamber volume (175 cm^3), t – saturation time, S – effective surface area of the samples, cm^2 , P and P_0 – final and initial pressure, atm [17].

Figure 3 shows the results of X-ray diffraction analysis. Ti reflexes and different compounds after titanium implantation are not detected. Only reflections of α -Zr with hexagonal lattice were observed after PIII with APF and PPF modes.

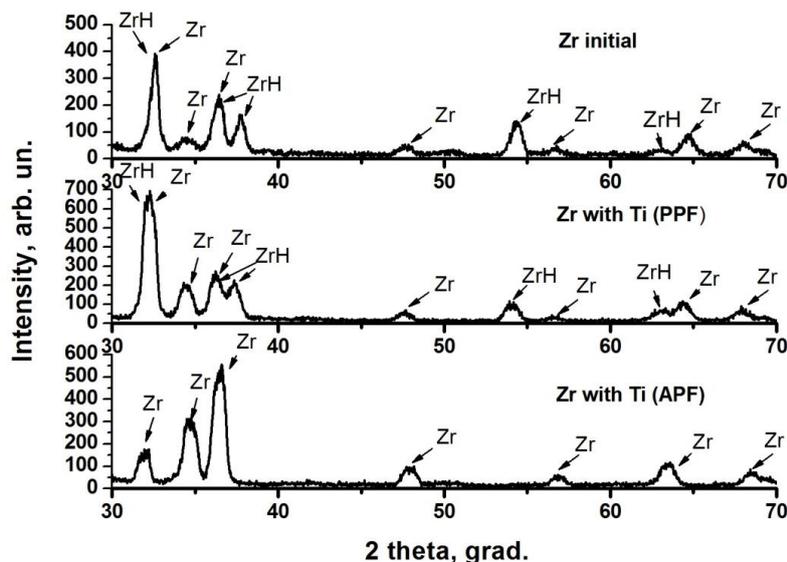


Figure 3. XRD analysis of Zr–2.5Nb after titanium implantation and hydrogen saturation. Zirconium hydride phases with tetragonal lattice are formed after hydrogen saturation in initial samples and Ti-implanted sample at PPF. Hydride phases in the sample modified with APF not

observed due to a low hydrogen concentration (206 ppm). Moreover, some concentration of hydrogen is in dissolved state.

Figure 4 shows the GDOES profiles of elements distributions in the modified layers after hydrogen saturation. Ti penetration depth into Zr–2.5Nb with APF is ~250 nm and with PPF is ~350 nm. The implantation with APF reduces the ion energy and dose of implanted material.

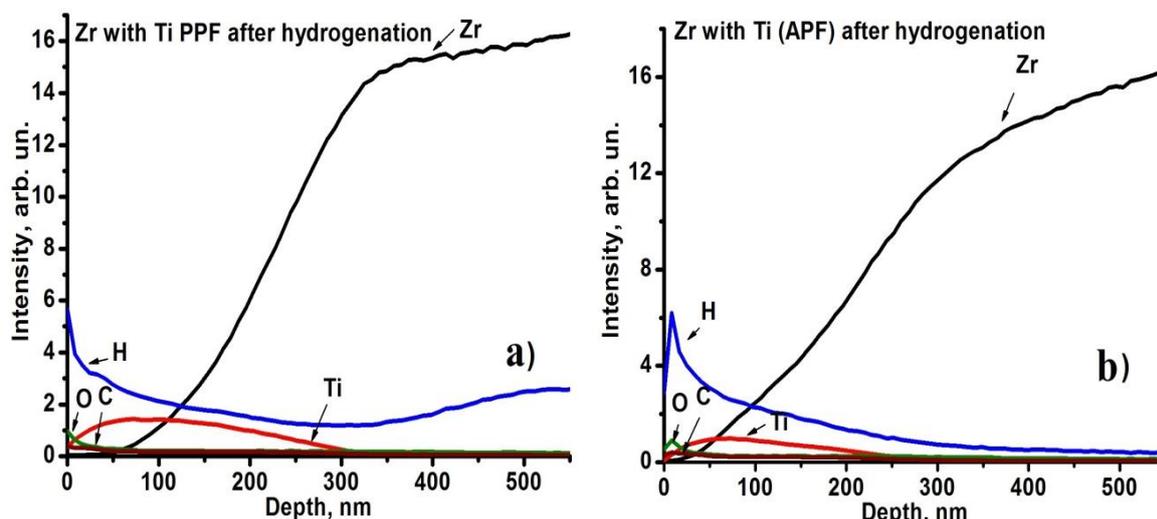


Figure 4. GDOES depth distribution of elements in Zr–2.5Nb after Ti implantation with APF (a) and PPF (b) after hydrogen saturation

Titanium implantation with APF significantly reduced hydrogen penetration into Zr–2.5Nb. The intensity of hydrogen signal monotonically decreased with increasing the depth and nearly reaches the intensity of hydrogen for the initial Zr–2.5Nb behind the modified layer with APF (Fig. 4a). However, the intensity of hydrogen increased behind the modified layer with PPF (Fig. 4b). This indicates the larger hydrogen concentration in the sample volume which confirmed by measured hydrogen concentration. Active plasma filtration more effectively reduced the amount of microdroplets formed in cathodic vacuum arc spots. Microdroplets can be pathways for hydrogen penetration into zirconium because it predominantly consists of metallic titanium [18] which has a high hydrogen absorption rate. Thus, hydrogen accumulates in the modified layer which is formed a diffusion barrier preventing hydrogen penetration into zirconium alloy.

Conclusion

PIII of titanium into Zr–2.5Nb reduces hydrogen absorption rate and total hydrogen concentration in the volume. The different radiation defects formed during titanium implantation can accumulate hydrogen primarily. When hydrogen fills the modified layer it begins to penetrate into Zr–2.5Nb volume by diffusion process. Titanium implantation with APF more effectively reduces hydrogen absorption by zirconium alloy in comparison with PPF. Intermetallic compounds were not observed in the experimental conditions.

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