Influence of surface structure on hydrogen interaction with Zr–1Nb alloy

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ABSTRACT

Modified structural-phase state in the surface layer ($\sim$10 µm) of Zr–1Nb alloy has been formed with the help of high-current pulsed electron beam. Surface treatment was carried out with energy density varied from 10 to 25 J/cm^2 and number of pulses varied from 1 to 10. We studied the dependence of hydrogen sorption and diffusion characteristics of Zr–1Nb alloy on its structure state at room temperature and at 350 °C.

1. Introduction

Studying the influence of different types of surface treatment on hydrogen diffusion and hydrogen sorption characteristics of metals and alloys is of primary importance for many industries, such as hydrogen energy, oil and gas industry and other areas dealing with structures operating in the conditions of hydrogen isotopes and hydrogen-containing medium exposure. On the one hand, such studies are of particular interest for the development of hydrogen storage materials. On the other hand, the characteristics of the aforementioned materials play a decisive role in choosing a method for increasing hydrogen resistance of materials. In particular, these studies are relevant to zirconium alloys that are usually applied in severe temperature, radiation and corrosive environment [1–3]. It is known that hydrogen permeability of metallic materials is heavily dependent on the surface state. It is possible to improve the catalytic activity and change hydrogen permeability either way by changing the composition or structural state of metal surface layers [4,5]. In this regard, surface modification by any existing method and study of hydrogen impact on the properties of modified metal is of great interest. Treatment by Low Energy High Current Pulsed Electron Beam (LEHCPEB) is the effective method for modification of metal properties [6–9]. Fast heating and subsequent cooling, propagation of shock waves, migration of vacancies and impurities induced by thermal gradients and radiation lead to a significant change of the structural phase state of surface layers (formation of metastable phases and surface nanostructuring) and to the modification of structure-dependent material properties. Such dramatic changes in surface layers of zirconium alloys have a significant impact on interaction of the material with hydrogen [10]. Thus,

the aim of the present work is also to investigate in detail the effects of the energy density and number of pulses on the microstructure evolution and hydrogen sorption of Zr–1Nb alloy.

2. Materials and methods

The study investigated the samples of Zr–1Nb zirconium alloy with the dimensions of 50 × 50 × 0.7 mm. The samples were irradiated by pulsed electron beam using Solo device located at the Institute of High Current Electronics of Siberian Branch of the Russian Academy of Sciences. Irradiation characteristics were as follows: number of pulses $N = (1–10)$, kinetic energy was equal to 18 keV, energy density Es = (5–25) J/cm^2. The samples were saturated by hydrogen using automated Gas Reaction Controller complex [11]. Hydrogenation was carried out at constant hydrogen pressure (2 atm) and temperature (350 °C) until reaching the hydrogen concentration of 500 ppm. Hydrogen permeability testing of samples was performed by electrochemical membrane method [12]. The samples before and after treatment were mechanically thinned to 100 µm. The study of electrochemical hydrogen permeation was performed in 1 M solution of sulfuric acid at the current density of 30 mA/mm^2 and room temperature. Hydrogen diffusion coefficient is determined using the formula Berrera [13]:

$$D = h^2/6t,\qquad(1)$$

where h is sample thickness and t is time of diffusion.

The structure and phase composition was analyzed using Philips SEM 515 scanning microscope and Shimadzu XRD 6000 diffractometer. The surface roughness was investigated using Hommel-Etamic T1000 profilometer.

3. Results and discussion

At the first stage, the regularities of changing properties and structure of samples irradiated by LEHCPEB were investigated. The results are shown in Fig. 1. The near-surface layer about 10 µm in depth with the modified structural-phase state was formed as a result of Zr–1Nb alloy treatment by a high-current pulsed electron beam. Pulsed electron beam irradiation and subsequent recrystallization of zirconium alloy lead to the formation of

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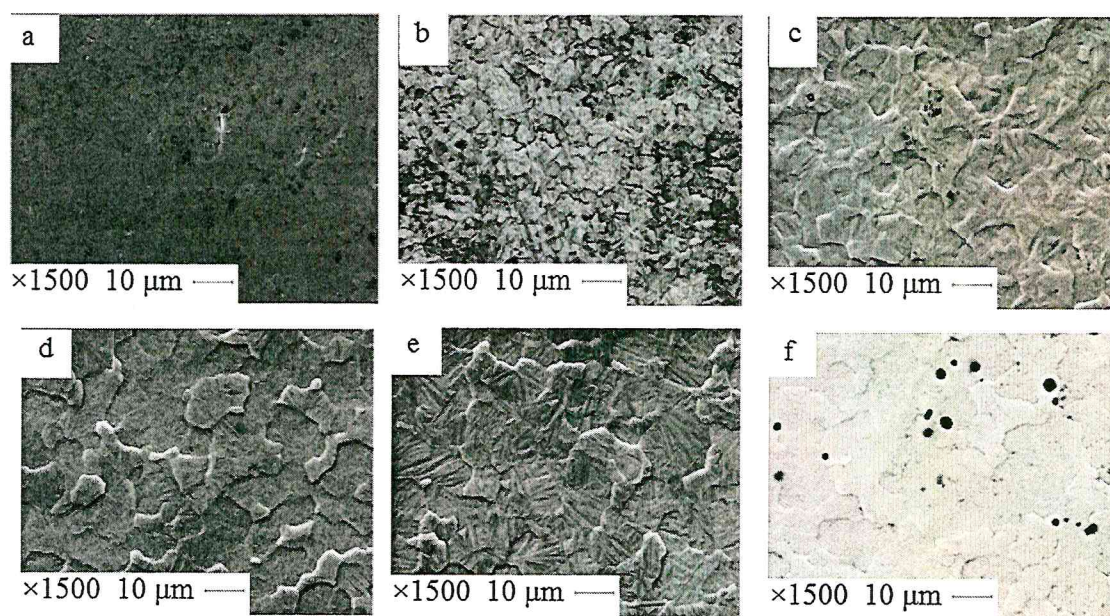 E-mail address: viktor.kudiiarov@gmail.com (V.N. Kudiiarov).

Fig. 1. Zr–1Nb surface microstructure (a) before and after treatment by LEHCPEB with energy Es = 18 J/cm² and different number of pulses: (b) N = 1, (c) N = 2, (d) N = 3, (e) N = 5 and (f) N = 10.
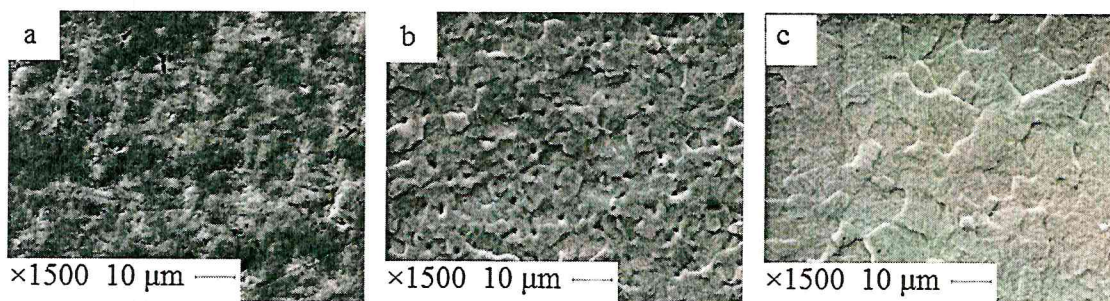

Fig. 2. Zr–1Nb surface microstructure after treatment by LEHCPEB, number of pulses N = 3 and (a) Es = 5 J/cm², (b) Es = 10 J/cm² and (c) Es = 25 J/cm².

structure with thin (needle) plates crossing the grain. It will be shown below that a high-speed cooling (10^7–10^8 K/s) of the irradiated samples resulted in the formation of complex morphology martensite in the surface layer. This fact is confirmed by SEM microscopy and XRD analysis. The XRD analysis showed that in Zr–1Nb alloy in the initial state in the whole interval of angles of incidence the lines of α-phase Zr with hexagonal lattice occur. The lattice parameters constituted a = 3.2357 A and c = 5.1471 A. After processing by LEHCPEB there is a decrease in the lattice parameters and the growth of internal elastic stresses (a = 3.2262 A and c = 5.1376 A).

Treatment by 1 pulse lead to the grain size reduction (Fig. 1b). The grain size before irradiation was 5–7 μm and after irradiation (for N = 1) it was 2–3 μm. The grain size increased with the further increase of number of pulses, i.e. for N = 2 it was 8–9 μm, for N = 3 it was 7.1–15 μm, for N = 5 it was 8.2–16.3 μm and for N = 10 it was 8–16.5 μm. Apparently, one of the reasons for this effect is the increase of melt lifetime. The samples modified by 5 and 10 pulses stand out due to high density of craters that are characterized by a wide range of dimensions varying from 1 to 5 μm (Fig. 1e and f). The formation of craters after irradiation was conditioned by the presence of target phase composition

inhomogeneities that initiated the process of local melting and evaporation of the surface.

The treatment by pulses with Es = 5 J/cm² (Fig. 2a) did not affect the surface structure, however, the roughness increased from Ra = 0.144 μm (samples before irradiation) to Ra = 0.178 μm (samples after irradiation). Grain size increased with the growth of energy density. The grain size was 4–8 μm for Es = 10 J/cm², 8.3–13.3 μm for Es = 10 J/cm² and 4.8–14 μm for Es = 25 J/cm².

Treatment of Zr–1Nb alloy by a high-current pulsed electron beam decreased the amount of hydrogen absorbed by the hydrogenated sample (Fig. 3 and Table 1). The rate of hydrogen sorption by Zr–1Nb samples before irradiation was 5×10^{-5} wt% per second. The lowest rate of hydrogen sorption (0.49×10^{-5} wt% per second) was observed after modification of samples by pulsed electron beam with Es = 18 J/cm² and N = 1. There is grain size reduction after this treatment. The change of energy density (5–10 J/cm²) of the beam had almost no effect on the rate of hydrogen sorption. The hydrogen sorption rates for Es = 5, Es = 10 and Es = 25 J/cm² are all higher than the sorption rates for Es = 18 J/cm². The reason of it would be researched additionally.

Earlier, it was noted that after the treatment by the beam with Es = 18 J/cm² and N = 10 there was a large number of craters
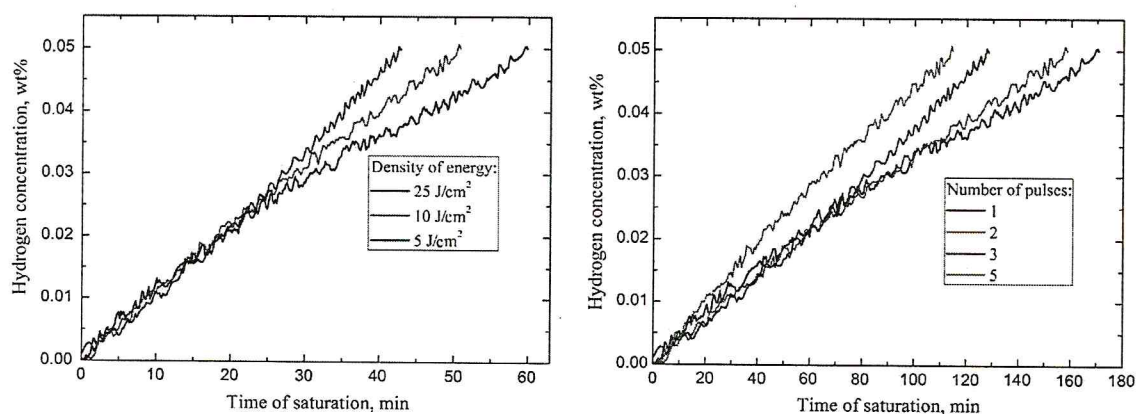
Fig. 3. Isotherms of modified Zr–1Nb alloy interaction with hydrogen at 350 °C.

Table 1

The rates of hydrogen sorption by Zr–1Nb samples at temperature of 350 °C after treatment by LEHCPEB.

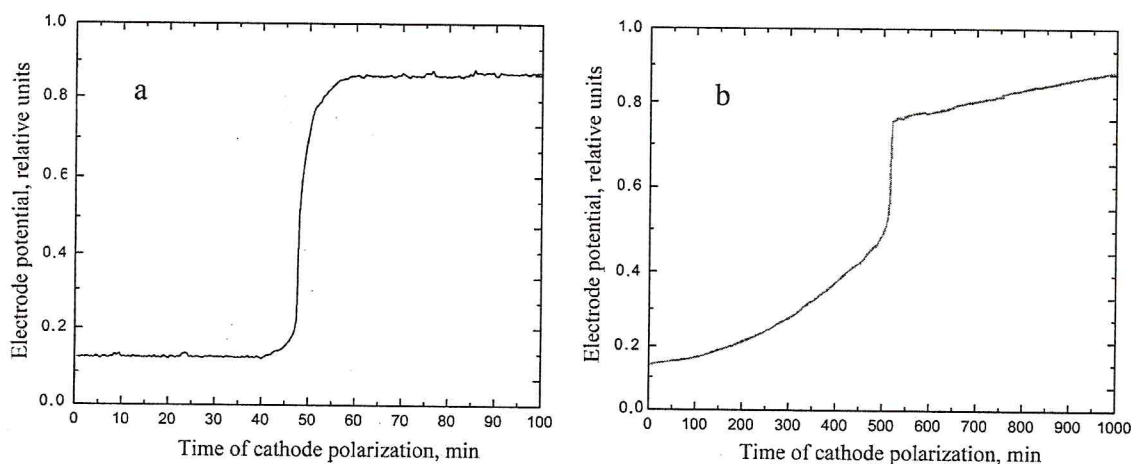| Treatment	Initial state	$N = 1$ pulsed Es = 18 J/cm^2	$N = 2$ pulsed Es = 18 J/cm^2	$N = 3$ pulsed Es = 18 J/cm^2	$N = 5$ pulsed Es = 18 J/cm^2	Es = 5 J/cm^2 $N = 3$	Es = 10 J/cm^2 $N = 3$	Es = 25 J/cm^2 $N = 3$
Hydrogen sorption rate, $\cdot 10^{-5}$ wt%/s	5	0.49	0.53	0.65	0.72	1.98	1.67	1.39

Fig. 4. Dependence of electrode potential on cathode polarization time for samples before (a) and after (b) irradiation by LEHCPEB.

detected on the surface of samples. Apparently, this effect is connected with the increasing rate of hydrogen sorption by samples in comparison with the other modes of treatment.

Fig. 4 represents the dependence of electrode potential on the cathode polarization time for samples before (a) and after (b) irradiation by a pulsed electron beam.

The sharp change of substance concentration (hydrogen ions) at the reference electrode in the equivalence point is obvious. This indicates that during the time interval of 45–55 min for non-irradiated sample, and 500–520 min for irradiated sample the hydrogen ions pass from anode cell to cathode cell. This time is referred to as the diffusion time. The values of the hydrogen diffusion coefficients can be estimated by using expression (1) for samples before and after irradiation as $\sim 5.5 \times 10^{-9}$ cm^2/s and $\sim 0.5 \times 10^{-9}$ cm^2/s respectively.

There is a high sensitivity of the hydrogen solubility and hydrogen diffusion rate to the structural inhomogeneities in the material according to [4]. Thus, the decreasing of hydrogen sorption rate and hydrogen diffusion coefficient is due to the formation of specific structure after treatment by LEHCPEB.

4. Conclusion

Treatment by LEHCPEB causes $\alpha^{/}$ martensitic structure formation in surface layer of the samples and grain size reduction. After treatment at $N = 5$ and 10 impulses there is high density of craters on the samples surface.

Hydrogen sorption rate and hydrogen diffusion coefficient decreases after zirconium alloy irradiation by LEHCPEB. While hydrogen sorption rate increases with increasing the number of pulses of LEHCPEB treatment.

Acknowledgment

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