

Effect of nonequilibrium hydrogen release in the ultrafine-grained Zr-1Nb alloy under the electron beam exposure

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Abstract. The evolution of structural and phase state and hydrogen release from the ultrafine-grained hydrogenated zirconium Zr-1Nb alloy during vacuum annealing and electron beams exposure were studied. The use of electron beam irradiation for hydrogen degassing is shown to decrease the temperature of active hydrogen release by 100–200 K and/or reduce the time required for hydrogen degassing from the alloy to concentrations corresponding to technical standards.

1. Introduction

Recently works on finding materials that can accumulate and store hydrogen are actively developed. It is known that hydride-forming metals and alloys in the ultrafine-grained (UFG) state can be effective solid-state hydrogen storages. However, the extraction of hydrogen from such materials generally occurs at elevated temperatures [1]. Therefore, the task is to reduce the temperature of the active hydrogen release from solid-state hydrogen storages. One of the possible problem solutions can be using the effect of nonequilibrium hydrogen release for hydrogen degassing. Electron beam irradiation of metals and alloys is known to activate hydrogen diffusion and desorption from the target material [2]. This leads to a significant lower-temperature shift of the peak in the curve for the temperature dependence of the dehydrogenation rate in metallic materials as compared to conventional thermal heating of the specimens in dynamic vacuum [3]. To activate the hydrogen release from the materials both continuous [3] and pulsed electron beams [4] can be used. In our opinion, pulsed electron beams irradiation is of particular interest. During pulsed electron beam irradiation the substantial heating occurs only near the surface of the material and the temperature in the bulk of the material varies slightly [5]. The latter is particularly important for the preservation of the UFG structure wherein recrystallization and grain growth are observed at temperatures of $(0.3-0.4)T_{\text{melt}}$ [6]. Taking into account the foregoing, the purpose of this work was to carry out comparative studies of the effect of vacuum annealing and pulsed and continuous electron beams exposure on the evolution of structural and phase state and hydrogen release from the UFG Zr-1Nb-H alloy.

2. Experimental Procedure

The experiment was performed using commercial Zr-1Nb alloy (E110 grade). The UFG state in the alloy was obtained by the method combining preliminary hydrogenation and hot plastic deformation



by pressing to 75–80 % at the temperature of 873 K [7]. Preliminary hydrogenation of the alloy to concentrations of 0.23 % (hereinafter, the hydrogen concentration is indicated in weight percent) was carried out by annealing in gas media using a Siverts' device at the temperature of 853 K. The hydrogen concentration in the samples was measured by RHEN602 gas analyzer with ± 0.0001 % accuracy.

Electron-microscopic investigation of thin foils was performed with the use of EM-125K transmission electron microscope. The size of structure elements was determined using the relevant micrographs by means of the secant method. The volume fractions and lattice parameters of the phases were obtained with the accuracy of $\pm 1\%$ and 0.0001 nm, respectively, using Shimadzu XRD7000 diffractometer with Cu-K α radiation source.

Test samples for annealing and irradiation were cut from billets by the electrospark method. Before testing the surface of samples were subjected to mechanical grinding and electrolytic polishing.

Hydrogen degassing of the samples was carried out in three ways: by annealing in a dynamic vacuum and by pulsed and continuous electron beams irradiation. Annealing in a dynamic vacuum was performed using a Siverts' device at 873 K. The heating rate to the annealing temperature was 10 K/s. Irradiation of the samples was conducted using «Solo» set-up with pulsed electron source [5]. Samples were irradiated by pulsed electron beam with the energy of (7–10) keV, pulse duration of 50 μ s and frequency of 2 Hz for (15–30) minutes. Beam diameter was equal to 10 mm. Continuous electron beam irradiation of the investigated samples was performed at the special set-up [4] at the following conditions: electron beam energy $E = 30$ keV, current on the sample $I = 35$ μ A. The sample was fixed on the heater and was placed in a vacuum chamber and then was preheated to temperatures of 628, 653, and 685 K for obtaining the hydrogen release dependences. The electron beam was turned on after stabilization of required temperature. Temperature and current were measured from the sample surface directly in the process of irradiation. Hydrogen release intensities depending on irradiation time was recorded with the use of bundled software, permitting to control the sweep of MH-7304 mass spectrometer and execute the linear heating of the samples with the rate of 1–10 K/s (in this experiment heating rate was 1 K/s).

3. Results and Discussion

The typical electron micrographs and corresponding electron diffraction patterns of the UFG structure of the Zr-1Nb-0.23H alloy are shown in Fig. 1. It is evident that an entangled deformational contrast is observed and some structure elements are poorly distinguished in the bright-field image of the structure (Fig. 1, a).

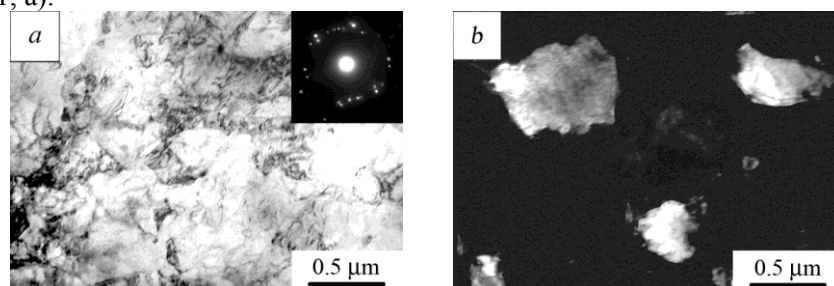


Figure 1. UFG Zr-1Nb-0.23H alloy microstructure, (a) bright field image, (b) dark field image

The electron diffraction patterns of the structure obtained for the area of $1.6 \mu\text{m}^2$ show an appreciable number of reflections uniformly distributed over a circle (Fig. 1, a). This is indicative of the presence of a large number of grain-subgrain structure elements in a unit volume and of their substantial misorientation. The average size of the grain-subgrain structure elements of the Zr-1Nb-0.23H alloy determined from the dark-field image (Fig. 1, b) was 0.4 μ m.

X-ray structure analysis demonstrated the Zr-1Nb-0.23H alloy in the UFG state has complicated phase composition. Alloy contains both main Zr_α phase and secondary phase Nb(Zr) (bcc) (reflections 1 – (100) and 2 – (200), Fig. 2, a). Particles of the secondary phase are located in the bulk and at grain

boundaries of Zr_{α} phase. Furthermore, $ZrH_{0.86}$ and $ZrH_{2.225}$ hydrides were detected in the UFG Zr-1Nb-0.23H alloy (reflections 3 – $(111)_{225}$, 4 – $(111)_{86}$, and 5 – $(200)_{86}$). It can be seen that $(220)_{86}$, $(311)_{225}$, and $(222)_{225}$ hydride reflections are superimposed on the (110) , (103) , and (112) reflections of the Zr_{α} phase. Apparently, some portion of hydrogen is present in solid solution of the Zr_{α} phase. This is indicated by the increase of its lattice parameters in Zr-1Nb-0.23H alloy after compaction in comparison with the initial fine-grained state.

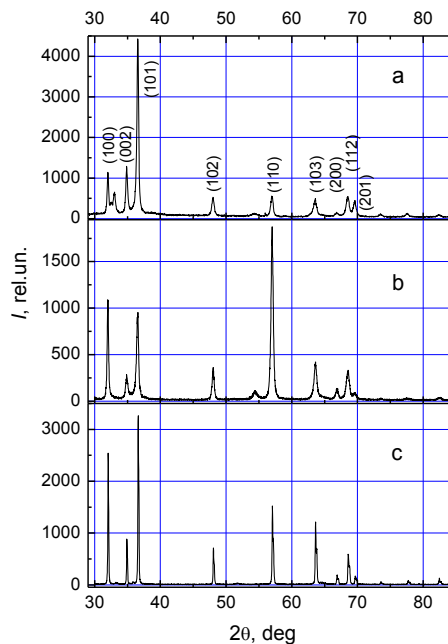


Figure 2. Portions of diffraction patterns for zirconium alloy samples: Zr-1Nb-0.23H (1); Zr-1Nb-0.115H (2); Zr-1Nb-0.00532H (3)

Temperature and time dependences of the hydrogen release from the UFG Zr-1Nb-0.23H alloy samples during dynamic vacuum annealing are shown in Fig. 3. It can be seen that hydrogen release from the alloy begins after heating to a temperature of ~ 623 K (Fig. 3, a).

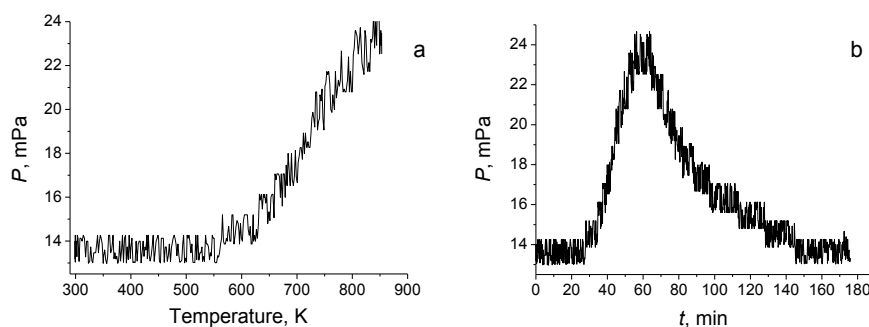


Figure 3. Temperature (a) and time (b) dependences of hydrogen release from the samples of the UFG Zr-1Nb-0.23H alloy during dynamic vacuum annealing

Maximum rate of hydrogen release is observed in the first 10 minutes after reaching the temperature of 873 K and during exposure at this temperature the rate of hydrogen release gradually decreases (Fig. 3, b). Measurement of residual hydrogen concentration showed its decrease from 0.23 to 0.115 % as a result of annealing by an indicated mode.

Table 1 shows the values of residual hydrogen concentrations in the Zr-Nb-H alloy after annealing at dynamic vacuum and pulsed electron beam exposure. It can be seen that after using modes of dynamic vacuum annealing hydrogen concentration in the Zr-Nb-0.23N alloy remains substantially greater than the concentration corresponding to the technical standards for this alloy (0.002–0.001 %).

At the same time use of pulsed electron beam allows not only to decrease the temperature and/or time of hydrogen degassing from the UFG alloy in comparison with annealing at dynamic vacuum, but in some modes to reduce the hydrogen concentration in alloy to the values closed to technical standards. In addition hydrogen concentration in the alloy decreases both in irradiated and non-irradiated parts of the sample. It should also be noted that after annealing at dynamic vacuum and pulsed electron beam irradiation the remaining hydrogen, apparently, is present mainly in the precipitations of the hydrides. This is indicated by the intensity growth of the (101), (110), and (103) reflections of the Zr_α phase, on which hydrides reflections are superimposed (Fig. 2, b).

Table 1. Hydrogen concentration in the UFG Zr-1Nb-0.23H alloy after annealing and electron beam irradiation

State of the UFG Zr-1Nb-H alloy		After annealing and in the irradiated part of the sample, %	In the non-irradiated part of the sample, %
Vacuum annealing	803 K, 60 min	0.178	
	823 K, 60 min	0.147	
	853 K, 60 min	0.087	
Pulsed electron beam irradiation	803 K, 15 min	0.0165	0.105
	823 K, 15 min	0.0266	0.119
	853 K, 15 min	0.0074	0.1
	803 K, 30 min	0.0036	0.0536
Continuous electron beam irradiation	823 K, 30 min	0.00187	0.00572
	657 K, 53 min	0.0227	
	698 K, 45 min	0.00532	

Four modes were used in the study of the continuous electron beam irradiation effect on hydrogen release from the UFG Zr-1Nb-0.23N alloy. Typical dependences of the intensity of hydrogen release from the alloy during continuous electron beam exposure on the temperature of preliminary (before the start of the electron beam irradiation) sample heating and the irradiation time are shown in Fig. 4.

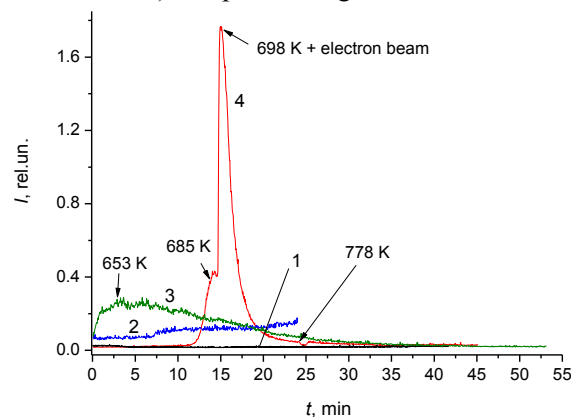


Figure 4. Typical dependences of the hydrogen release intensities on the preheating temperature and irradiation time: 1 – continuous electron beam exposure without preheating; 2 – heating to 628 K; 3 – preheating to 628 K and exposure of continuous electron beam; 4 – preheating to 685 K and exposure of continuous electron beam

It can be seen that hydrogen degassing performed by means of electron beam irradiation without preheating does not lead to any significant changes in the hydrogen content in the alloy (mode 1, Fig. 4, curve 1). In the case of the preliminary sample heating to 628 K, its temperature under electron beam exposure increases to 665 K and hydrogen starts to release from alloy (mode 2, Fig. 4, curve 2). However, the intensity of hydrogen release is insignificant. The preheating temperature rise by 25 K leads to a sharp increase in the intensity of hydrogen release from the alloy with a slight changing the

sample temperature (from 653 to 657 K) after electron beam switching (mode 3, Fig. 4, curve 3). During further irradiation for 45 min sample temperature does not change and hydrogen release intensity gradually decreases (practically to zero). Hydrogen concentration in alloy after irradiation by mode 3 decreases 10 times (to 0.0227 %). Gradual sample heating to the initial temperature of hydrogen release (685 K) was used for the irradiation mode 4. As curing time at the temperature increases the intensity of hydrogen release begins to decrease (Fig. 4, curve 4). Beginning of electron beam exposure leads to a rise in sample temperature to ~ 698 K and significant growth of hydrogen release intensity (Fig. 4, curve 4). During the further 5 min of irradiation the decrease of hydrogen release intensity practically to zero is observed, and for subsequent 20 min of irradiation, it is not changed. For the total time of heating and electron beam exposure in the indicated mode (~ 45 min) hydrogen concentration in the UFG alloy decreases from 0.23 to 0.00532 %. In this case no hydride precipitations are observed in the material (Fig. 2, c).

Structure examinations of Zr-1Nb-0.23H alloy revealed that during vacuum annealing and exposure of pulsed and continuous electron beams growth of grain-subgrain UFG structure elements occurs. Thus, after annealing at 853 K, 60 min the average size of structure elements increased to ~1.3 μm . During irradiation by pulsed and continuous electron beams the rate of growth of the grain-subgrain UFG structure elements increased in comparison with annealing. In the case of pulsed electron beam exposure at 853 K the average size of grain-subgrain structure elements increased to ~1.2 μm for 30 min. Continuous electron beam irradiation at 698 K for 60 min results in increase of average size of structure elements to 0.67 μm . At the same time alloy annealing in dynamic vacuum for 60 min even at indicated temperature does not lead to change of the average size of structure elements. Observed fluctuating of growth rate of UFG structure elements of the Zr-1Nb-H alloy under electron beams irradiation is apparently connected with the activation by electron beam not only hydrogen diffusion, but also diffusion of other elements.

4. Conclusion

Thus, as exemplified by the hydrogenated to a concentration of 0.23% Zr-1Nb alloy, both pulsed and continuous electron beam irradiation can be used for hydrogen degassing from the metallic hydride-forming materials. It was found that exposure of pulsed and continuous electron beams allows to decrease the temperature of the active hydrogen release by 100–200 K and/or reduce the time required for hydrogen degassing from the alloy to concentrations corresponding to technical standards.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (project No. 15-08-03823).

References

- [1] Il'in A A, Kolachev B A, Nosov V K, and Mamonov A M 2002 *Vodorodnaya tekhnologiya titanovykh splavov* (Moscow: MISIS) p 392
- [2] Tyurin Yu I and Chernov I P 1999 *Dokl. Ros. Akad. Nauk* **3** 328
- [3] Nikitenkov N N, Kudryavtzeva E N, Chernov I P, Tyurin Yu I, Grabovetskaya G P, Melnikova E N 2008 *Proc. 9 Int. Conf. on Modification of Materials with Particle Beams and Plasma Flows* (Tomsk) p 316
- [4] Stepanova E N, Grabovetskaya G P, Mishin I P, Chernov I P, Teresov A D 2013 *Izvestia visshih uchebnykh zavedenii. Fizika* **56** 95
- [5] Koval N N, Grigoryev S V, Ivanov Yu F, Ovcharenko V E, Kolubaeva Yu A, Teresov A D 2009 *IEEE Trans. Plasma Sci.* **37** 1998
- [6] Kolobov Yu R, Valiev R Z, Grabovetskaya G P, Zhilyaev A P, Ivanov M B, Dudarev E F, Kashin O A, Ivanov K V, Naidenkin E V 2001 *Grain boundary diffusion and properties of nanostructured materials* (Novosibirsk: Nauka) p 232
- [7] Grabovetskaya G P, Stepanova E N, Ratochka I V, Naidenkin E V, Lykova O N 2013 *Inorganic Materials: Applied Research* **4** (2) 92