

FEATURES OF ULTRAFINE-GRAINED STRUCTURE FORMING IN Zr-1Nb ALLOY

Ekaterina N. Stepanova, Galina P. Grabovetskaya*, Ivan P. Mishin*, Konstantin A. Prosolov
National Research Tomsk Polytechnic University, Lenin Avenue 30, Tomsk, 634050, Russia
Institute of Strength Physics and Materials Science of Siberian Branch of Russian Academy of
Sciences, Akademicheskoy Avenue 2/4, Tomsk, 634021, Russia

Abstract

Ultrafine-grained structure forming by the method combined reversible hydrogenation and hot pressing in Zr-1Nb alloy was investigated. Preliminary hydrogenation to concentrations of (0.14–0.4) % at 873 K is found to lead to yield strength decreasing in Zr-1Nb alloy during hot pressing by 1.5–2 times. During uniaxial compression at (70–72) % under isothermal conditions at a temperature of 873 K in Zr-1Nb alloy, hydrogenated to concentration of 0.22 %, homogeneous ultrafine grained structure with an average grain size of 0.4 μm was formed.

Key words: zirconium alloy, ultrafine-grained structure, hydrogen

INTRODUCTION

The formation of ultrafine grained (nano- and submicrocrystalline) states in metals and alloys is known to improve significantly not only the level of their strength characteristics, but often to provide the creation of properties complex that are required to work under certain conditions. Analysis of published data showed the possibility of ultrafine grained state forming in metallic polycrystals by severe plastic deformation, leading to increase of the material strength characteristics and satisfactory plasticity, increase of hydrogen embrittlement resistance and hydrogen concentration in the alloy, corresponding to the material transition to brittle fracture (Meyers, Mishra & Benson 2006; Kolobov et al. 2001; Noskova & Mulyukov 2003; Zhu & Langdon 2005; Grabovetskaya et al. 2013).

One of the often used techniques of ultrafine grained structure formation is such severe plastic deformation method as three dimensional pressing at elevated temperatures, making it possible to form ultrafine grained grain/subgrain structure with dimensions of the elements of (0.1–0.5) μm . An advantage of this method is the possibility of using a simple pattern of deformation without the necessity of application of complicated special tooling (pressing tool). In turn, the main disadvantage of this method is looping of the “heating–hot pressing” (upsetting) cycle to achieve the dimensions of the structure elements indicated above and significant material cost. At the same time method built upon reversible hydrogen treatment and hot plastic deformation is known to reduce the deformation resistance and decrease the number of cycles (amount of deformation) for hydride-forming materials during three dimensional pressing of titanium alloys in order to form ultrafine grained structure (Murzinova & Salishchev 2008; Grabovetskaya et al. 2006). This is due to the using of phase transformations initiated by hydrogen presence in the alloy. However, depending on the material characteristics (stacking fault energy, the possibility of twinning or martensite transformation, temperature interval of diffusion-controlled process), the value of ultrafine grained structure elements, and hence it's properties may be different for different metals and alloys, even at the same pressing modes and hydrogen concentrations in the material. Therefore research of the of structural and phase state evolution during ultrafine grained structure forming with the use of initiated by hydrogen

presence phase transformations in the materials on which such studies have not been conducted is urgent and important.

A purpose of this work is investigation of the hydrogen concentration effect on the evolution of structural and phase state of commercial Zr-1Nb alloy in forming ultrafine-grained structure by the method built upon reversible hydrogenation and hot plastic deformation.

The assumption that application of the method combining the reversible hydrogenation and hot plastic deformation for obtaining an ultrafine structure in the zirconium alloys, is based on the diagrams similarity of Ti-H and Zr-H and in the presence both in zirconium and titanium polymorphic β/α transformation (Lyakishev 1997; Borisova, Bochvar & Brun 1982; Zaimovskii, Nikulin & Reshetnicov 1994).

TEST MATERIAL AND INVESTIGATION TECHNIQUES

The commercial Zr-1Nb alloy with the hydrogen content of 0.002 % (hereinafter, the hydrogen concentration in the alloy is stated in wt %) was used as a material for the investigation. Samples of the alloy in the initial state that were used in the work have a cylindrical shape with dimensions: diameter of 20 mm, height of 30 mm.

Hydrogen alloying of the alloy up to concentrations of (0.14–0.4) % was carried out in gas media by a Siverst type apparatus at temperature of 973 K. The hydrogen concentration in the samples was measured by a RHEN 602 gas analyzer with 0.001 % accuracy. After alloying samples were homogenized by annealing in a helium atmosphere for 8 hours at a temperature of 873 K. After homogenization samples were quenched in water.

Deformation of preliminary hydrogenated samples by 70–72 % was performed in isothermal conditions at a temperature of 873 K ($0.41T_{\text{melt}}$) in accordance with a schedule of single uniaxial compression with initial speed of $1.5 \cdot 10^{-2} \text{ s}^{-1}$.

Microscopic examination of thin foils was performed under optical microscope AXIOVERT-200MAT (Zeiss, Germany) and an EM-125K transmission electron microscope. The size of structure elements was measured from the relevant micrographs by means of the secant method. The phase composition of the alloy was defined by the X-ray diffraction method using a Shimadzu XRD6000 diffractometer in Cu K_α radiation.

Pressing and compression test were carried out at the special facility, equipped with automatic recording of the load-time curve.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Investigated zirconium Zr-1Nb alloy in the initial state has nonequiaxial fine-grained structure with a grain size of 3-5 and 6-10 μm in transverse and longitudinal sections, respectively. At the grain boundaries and in the volume of grains particles with a sizes vary from a few tens of nanometers to a few micrometers are observed (Fig. 1, a).

There is also a crystallographic texture in the alloy (Fig. 1, b). The preferential crystallographic direction [100] of Zr_α phase coincides with the longitudinal axis of the cylinder.

Hydrogenation to concentrations of (0.13–0.4) % does not change the grain size, but leads to the phase composition changing in the alloy (Fig. 2). In addition to the above-mentioned phases precipitations of hydrides ZrH_{-86} и ZrH_{-225} with a pronounced texture appear in the alloy. This is most clearly

appeared in the alloy Zr-1Nb-0,4H (Fig. 2, b). Prevailing crystallographic directions [220] of ZrH-86 hydride and [311] of ZrH₂-225 hydride coincide with the longitudinal axis of the cylinder. The diffraction reflections (220) of ZrH-86 hydride and (311) of ZrH₂-225 hydride are superimposed on the reflections (110) and (103) of Zr_α phase, respectively (Fig. 2, b).

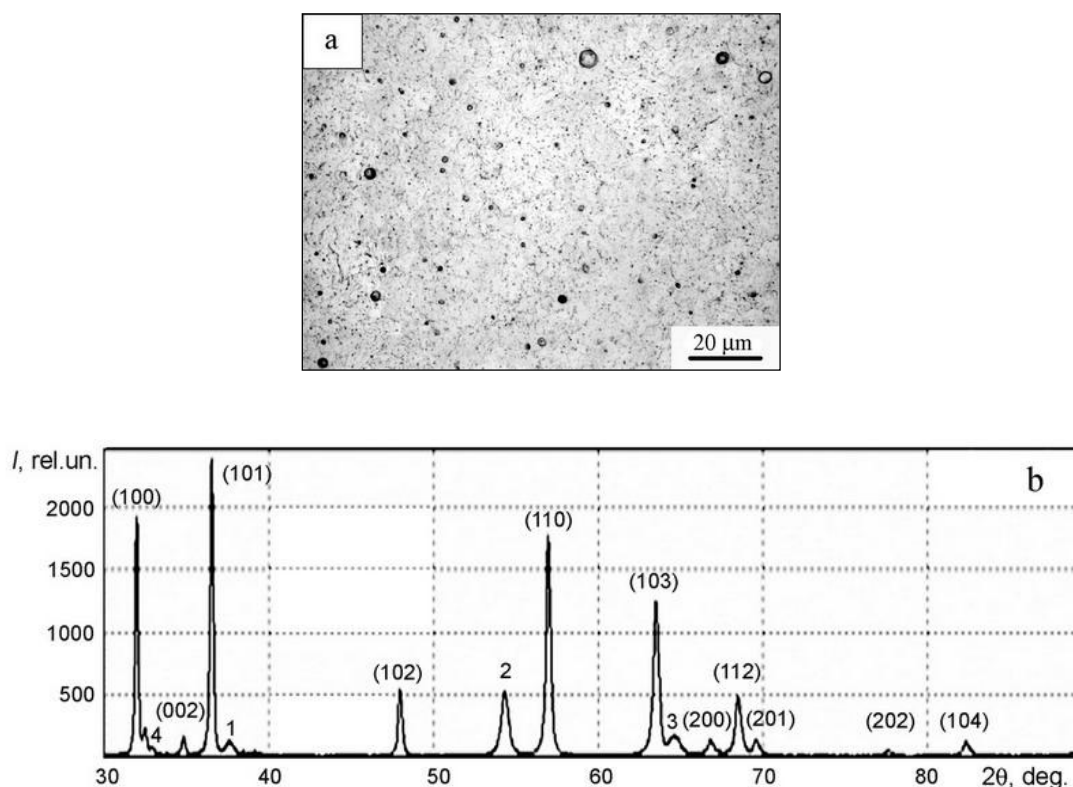


Fig. 1. Microstructure (a) and diffraction portions (b) of zirconium Zr-1Nb alloy

X-ray diffraction studies of the samples after homogenization and subsequent quenching in water from the homogenization temperature (873 K) showed that their phase composition is similar to the phase composition of the alloy in the initial state (Fig. 2, c). However reflections on the diffraction portions of Zr-1Nb-H alloys specimens after homogenization and subsequent quenching have a greater width in comparison with unquenched samples and slightly shifted towards smaller angles, indicating the hydrogen presence in the solid solution.

The structure of Zr-1Nb-H alloy samples quenched in a water from the homogenization temperature and containing (0.13–0.4) % of hydrogen has the lamellar character (Fig. 3). However, the plate's dispersion of this structure is determined by the hydrogen concentration in the alloy. The most dispersed lamellar structure is formed in an alloy containing 0.22 % of hydrogen (Fig 3, b).

It was determined by pressing of the quenched samples that the yield strength of the Zr-1Nb-H alloy nonmonotonically depends on the hydrogen concentration (Fig. 4). The alloy with a hydrogen content of 0.002 % has the highest yield strength. As the concentration of hydrogen in the alloy is increasing, yield strength initially decreases and then increases.

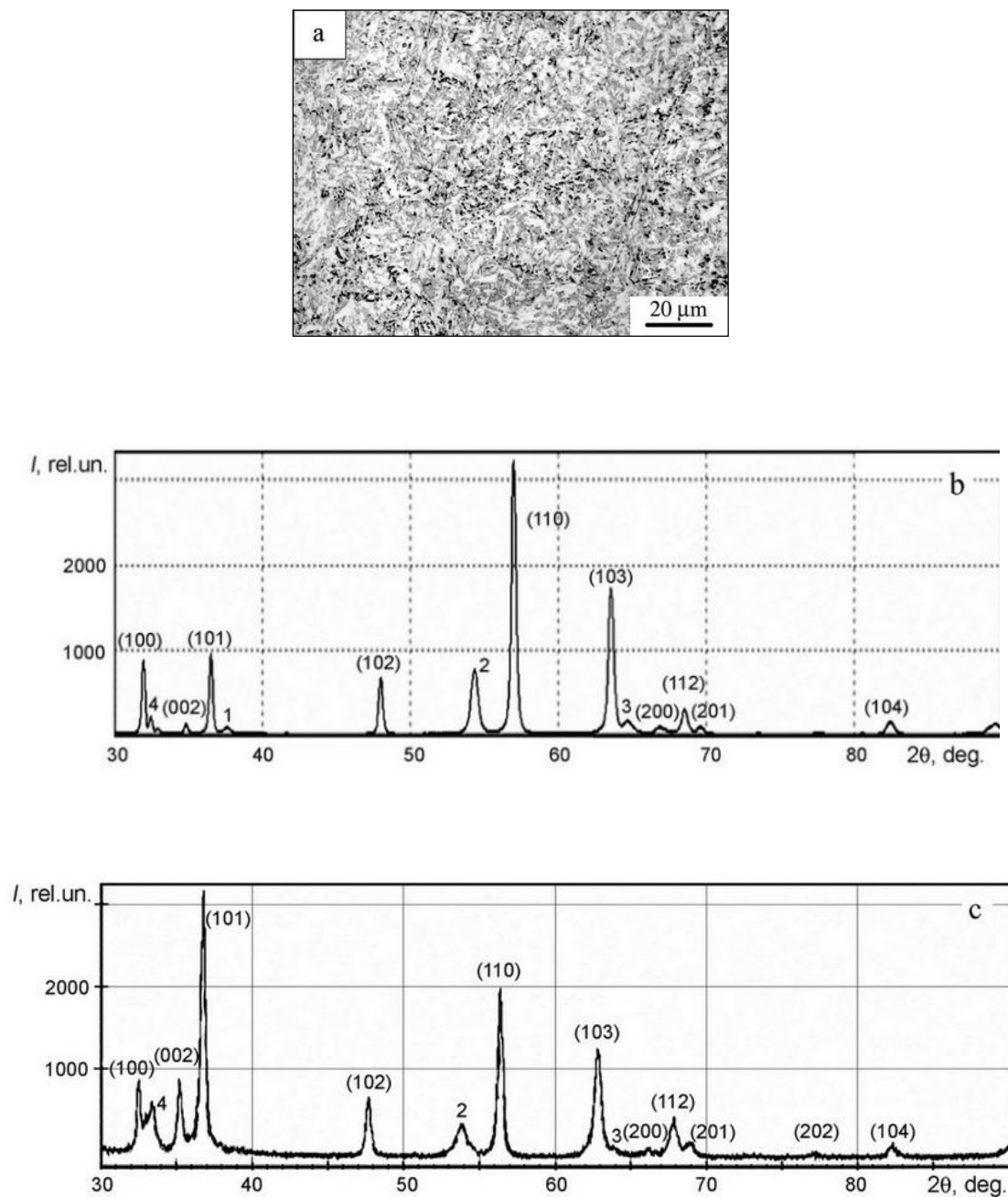


Fig. 2. Microstructure (a) and diffraction portions (b – samples after hydrogenation, c – samples after homogenization and subsequent quenching in water from the homogenization temperature) of zirconium Zr-1Nb alloy hydrogenated to 0.4 %

Presence of minimum on the curve of the yield strength on the hydrogen concentration in the alloy is apparently connected with two antagonistic factors: increasing in the alloy volume fraction of the less hard β_{Zr} phase with the increasing of hydrogen concentration and solid solution phase hardening by the

hydrogen. At low hydrogen concentrations in the alloy the first factor has a decisive influence on the value of yield strength, at high concentrations – the second one prevails. A similar effect of hydrogen on the value of yield stress is observed in titanium based alloys [Murzinova & Salishchev 2008].

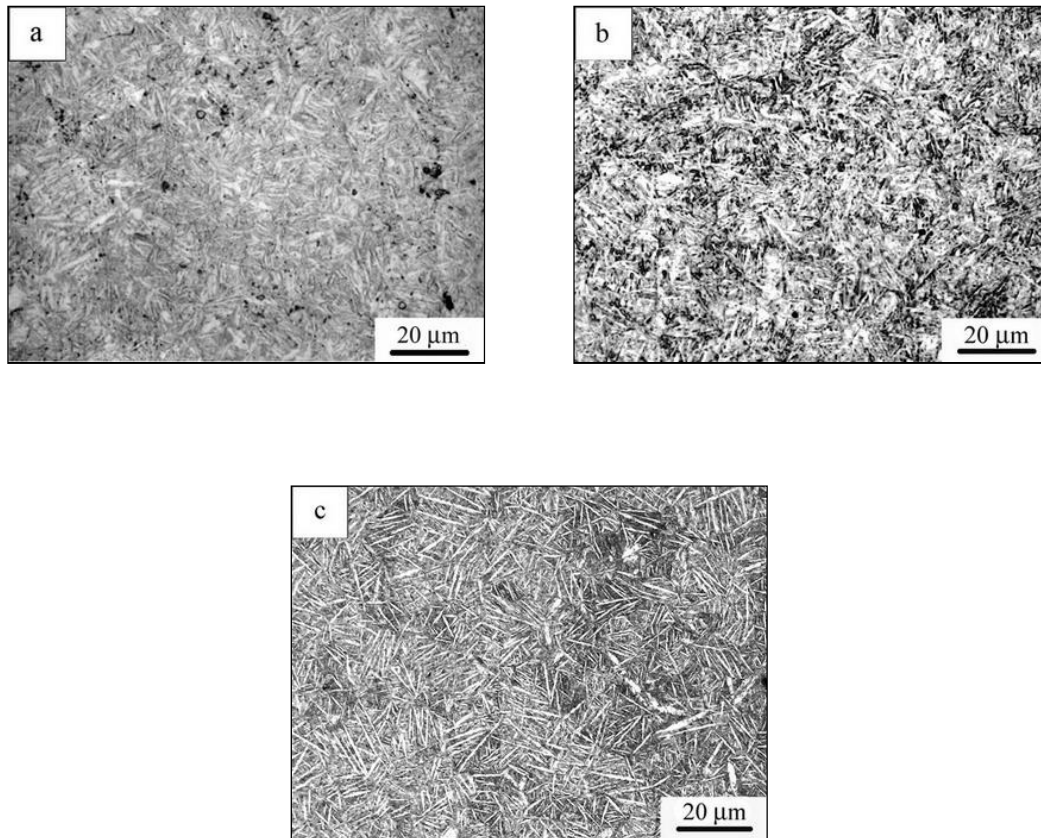


Fig. 3. Microstructure of zirconium Zr-1Nb-H alloy with different hydrogen content
after quenching from a temperature of 873 K
a – 0,14 %; b – 0,22 %; c – 0,4 %

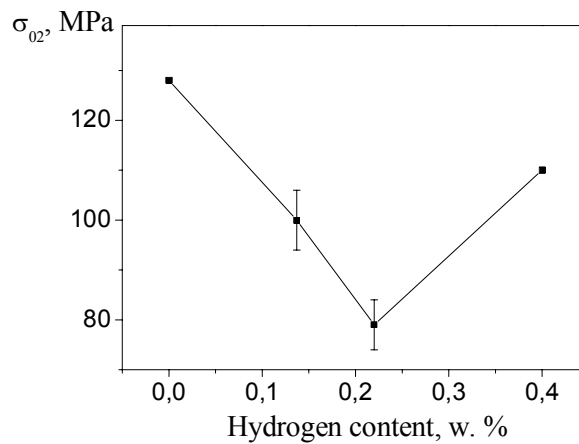
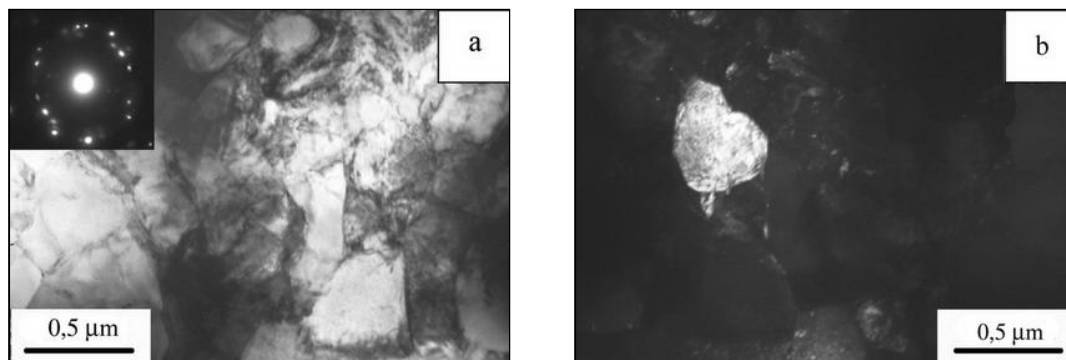


Fig. 4. The dependence of the yield strength on the hydrogen content in the Zr-1Nb alloy under compression at 873 K

Electron-microscopic studies of the Zr-1Nb-H alloy structure after pressing demonstrated that the character of the structure being formed in a single pressing at a temperature of 873 K to (70–72) % also depends on the hydrogen concentration in the alloy. Figure 5 shows a typical structure of the Zr-1Nb-0.14H alloy after pressing. On the light-field image of the alloy structure complex deformation contrast does not allow to reveal structure elements. A dark-field image shows that as a result of hot pressing the uniform ultrafine grained structure is formed in Zr-1Nb-0.14H alloy. Along with the grain-subgrain structure elements with dimensions of (0.1–0.4) μm with preferably large angle grain boundaries (Fig. 5, b) there are grains in the structure with the grain size of about 1 μm . The internal structure of such grains is fragmented.



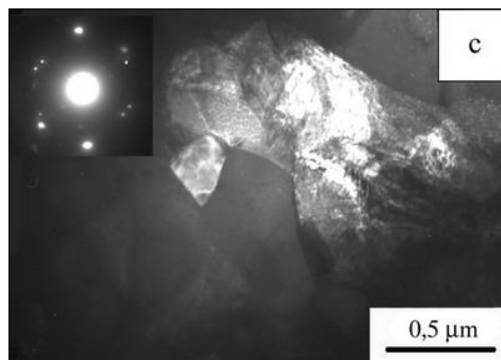
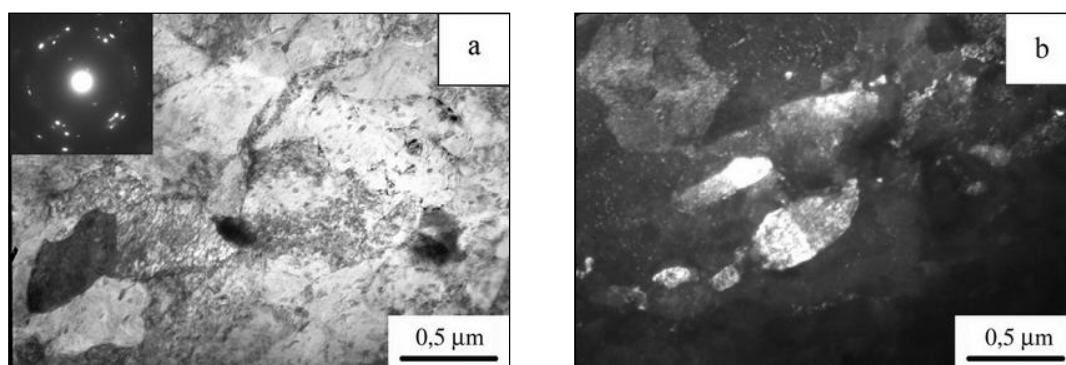


Fig. 5. Electron micrographs of the Zr-1Nb-0.14H alloy structure after single-stage compression to 72 %: a – a light-field image; b and c – a dark-field image

Increase of hydrogen concentration to 0.22 % results in more uniform ultrafine grained structure forming in the alloy by pressing (Fig. 6). The electron diffraction patterns of the structure obtained for an area of $1.2 \mu\text{m}^2$ show an appreciable number of reflections evenly distributed over a circle. 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 size of structure elements varies between 0.1 and $0.65 \mu\text{m}$ (Fig. 6, b). The average size of grain-subgrain structure elements found from dark-field images is $0.4 \mu\text{m}$. The phase composition of the Zr-1Nb-0.22H alloy is identical with that of the initial Zr-1Nb-0.002H alloy (Fig. 6, c). At the same time, there is no any texture in the [100] direction in the structure, but there is a slight (March-Dolase coefficient is 0.77) texturing along the [101] direction.

Formation of homogeneous ultrafine grained structure by a single compression of the lamellar structure to 72 % reduction in the alloy containing 0.4 % of hydrogen was not achieved. In this alloy after deformation to 72 % reduction at 873 K along with grains having submicron sizes we observed lamellar particles with a width of less than $1 \mu\text{m}$ and a length of a few micrometers (Fig. 7). This is presumably caused by the presence of coarse lamellar structure in the alloy before hot pressing.

Thus, performed research has shown that the most homogeneous ultrafine grained structure with an average size of grain-subgrain structure elements of $\sim 0.4 \mu\text{m}$ is formed in the Zr-1Nb alloy, containing 0.22 % of hydrogen, with the use of above-mentioned deformation mode.



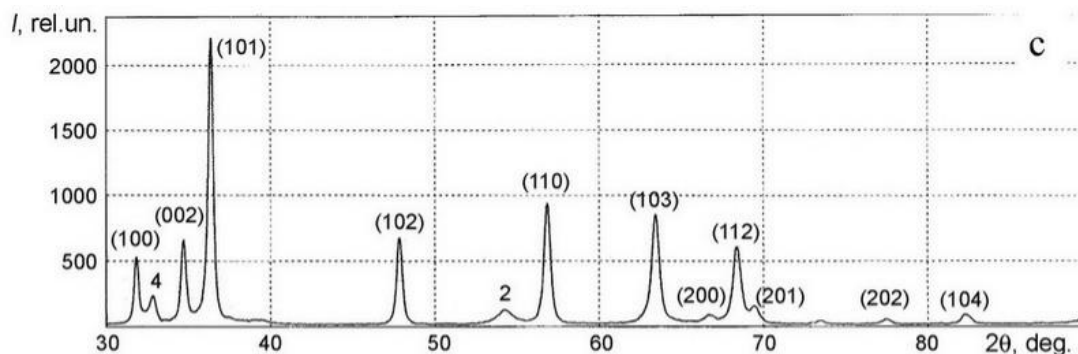


Fig. 6. Electron micrographs of the Zr-1Nb-0.22H alloy structure after single-stage compression to 72 %: a – a light-field image; b – a dark-field image; c – portion of diffraction patterns

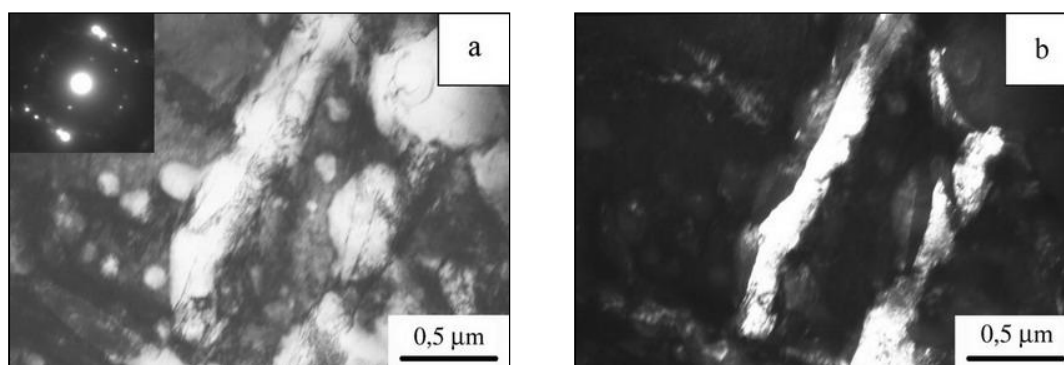


Fig. 7. Electron micrographs of the Zr-1Nb-0.4H alloy structure after single-stage compression to 72 %: a – a light-field image; b – a dark-field image

Hydrogen presence in zirconium alloys is known to lead to hydrogen embrittlement (Zaimovskii, Nikulin & Reshetnicov 1994). Therefore, after ultrafine grained state forming hydrogen should be completely removed from the alloy. The most common method for hydrogen removing from metallic materials is dynamic vacuum annealing. Removal of dissolved hydrogen from titanium and zirconium alloys accompanied $\beta \rightarrow \alpha$ transformation.

Thus, depending on the hydrogen concentration, heating conditions and annealing temperature the additional refinement of the microstructure or grain growth of α phase can be observed (Ilyin et al. 2002). In this work hydrogen was removed from Zr-1Nb-0.22H alloy by annealing in a dynamic vacuum at 873 K for 1.5 hour. Measurement of hydrogen concentration showed that the residual hydrogen concentration in the alloy (~ 0.008 %) after mentioned annealing is higher in comparison with its initial state (0.002 %). In addition, alloy structure research showed that during vacuum annealing at 873 K growth of α phase grains to (1–3) μm occurs.

CONCLUSIONS

Preliminary hydrogenation to concentrations of (0.14–0.4) % at 873 K leads to yield strength decreasing in Zr-1Nb alloy during hot pressing by 1.5–2 times. During uniaxial compression at (70–72) % under isothermal conditions at a temperature of 873 K in Zr-1Nb alloy, hydrogenated to concentration of 0.22 %, homogeneous ultrafine grained structure with an average grain size of 0.4 μm was formed. However, the hydrogen removal by annealing in a dynamic vacuum at a temperature of 873 K results in grain growth in the alloy from submicron to micron size.

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