

## EFFECT OF HYDROGENATION ON CREEP AND STRUCTURE EVOLUTION OF NANOCRYSTALLINE Zr1Nb ALLOY

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The regularities of creep, mechanical characteristics, and structure evolution of Zr1Nb nanocrystalline alloy obtained by intensive plastic deformation and hydrogenated from a gaseous medium are studied. It is shown that, due to deformation under creep conditions, a small amount of zirconium hydrides is formed in the structure of the Zr1Nb alloy, which has little effect on its strength properties and ductility. The observed features of the creep characteristics are mainly due to the past relaxation of internal stresses and the corresponding structural transformations during hydrogenation and subsequent deformation.

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### INTRODUCTION

Zirconium alloys are widely used in the nuclear power industry as a structural materials for fuel rod cladding in nuclear reactors. During exploitation, the fuel rod claddings operate in difficult conditions with the simultaneous action of irradiation, high temperature, corrosive environment and mechanical stresses [1, 2]. Therefore, the fuel rod cladding material must have good mechanical properties, corrosion resistance, and radiation growth resistance.

The critical processes that limit the service life of reactor materials include their hydrogenation [3]. Hydrogen diffusing in the crystal lattice of a metal is able to interact with various kinds of defects contained in real solids [3, 4]. The hydrogenation of metals strongly depends on the deformation of the lattice, the nature of the dislocation structure, and the appearance of point defects. Deformation can lead to a decrease or increase in the volume of hydrogen collectors, and, accordingly, change the absorption capacity of metals. In this case, microcavities and blisters have the greatest effect on the capture of hydrogen [4, 5].

Hydrogen, either in a solid solution or in the form of a hydride, causes embrittlement of metals and alloys. Hydrogen embrittlement of zirconium alloys is one of the most important safety issues for nuclear power plants using light water reactors and the main cause of mechanical degradation of fuel cladding [6–8].

Hydride precipitates reduce the ability of the material to plastic deformation and reduce its crack resistance. The degree of reduction in the plasticity of a hydrogenated alloy depends on the concentration of hydrogen, temperature, size, morphology of hydrides and their orientation with respect to the applied stresses. In this case, the factors of temperature and orientation are most often decisive. The greatest embrittlement is caused by lamellar precipitates oriented perpendicular to the direction of acting stresses [6]. The formation of hydrides leads to the formation of microcracks at interfacial boundaries.

Studies have shown that hydrogen does not significantly affect the strength characteristics of zirconium and its alloys, but considerably reduces its

impact strength at low temperatures. Hydrogen embrittlement manifests itself at a content of 0.001% H<sub>2</sub> and manifests itself more intensely, the higher the hydrogen content [7, 8].

The purpose of this work is to study the regularities of creep and evolution of the nanostructure of the Zr1Nb alloy obtained by intensive plastic deformation (IPD) and the effect on its mechanical characteristics and structure of hydrogenation.

### MATERIAL AND PROCESSING METHOD

An ingot of Zr1Nb alloy obtained by electron beam melting was cut into templates and deformed by combined rolling at 77...300 K to the true strain value of  $\varepsilon \sim 3.9$ . Samples 3×0.2×50 mm in size were mechanically cut from rolled strips. The chemical composition of the alloy under study is given in [9]. In order to study the effect of hydrogenation on the structure and properties of the alloy, processing was carried out in the following modes:

1. MT-1 – rolling deformation, final strain  $\varepsilon \sim 3.9$ ;
2. MT-2 – MT-1 + hydrogenation.

Samples were saturated with hydrogen on an automated setup based on a helium leak detector. The sample was placed in a chamber, the pressure in which was pumped out to 0.013 Pa, after which hydrogen was injected into it at a pressure of  $\sim 0.05$  MPa. The sample was continuously heated at a rate of 8 K/min to a temperature of 680 K, kept at this temperature for 5 h, and the pressure in the chamber was measured. The amount of absorbed gas was determined from the pressure difference in the chamber before and after saturation by the gravimetric method, as well as from the dependence of the intensity of hydrogen yield on temperature during uniform heating of the samples, and its amounted to 0.09 wt.%

Creep tests were carried out in the step loading regime at a temperature of 300 and 680 K, the measurement accuracy was  $\sim 5 \cdot 10^{-5}$  cm. The electrical resistance (R) was measured at room temperature by the compensation method. The structure evolution control was carried out using the electron microscopic method.

## RESULTS AND DISCUSSION

Fig. 1 and Table show the dependences of the creep rate at 300 and 680 K and the mechanical characteristics of Zr1Nb alloy samples after rolling and after hydrogenation in the entire studied stress range.

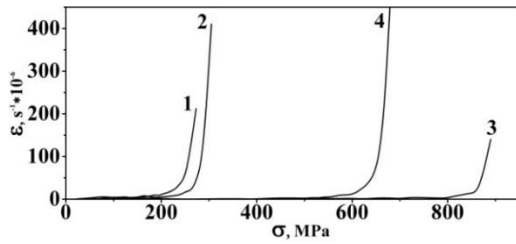


Fig. 1. Creep rates at  $T = 300$  K (3, 4) and 680 K (1, 2) as a function of the true stress for the samples of Zr1Nb alloy subjected to different treatments: 1, 3 – MT-1; 2, 4 – MT-2

Mechanical characteristics of Zr1Nb alloy samples after various treatments

Test temperature	Modes of treatment	$R_{300}/R_{77}$	$\sigma_{0.2}$ , MPa	$\sigma_B$ , MPa	$\epsilon$ , %
300 K	MO-1	3.52	812	890	7.3
	MO-1+H <sub>2</sub>	3.86	567	685	7.4
680 K	MO-1	3.52	187	273	10.9
	MO-1+H <sub>2</sub>	3.86	201	305	11.0

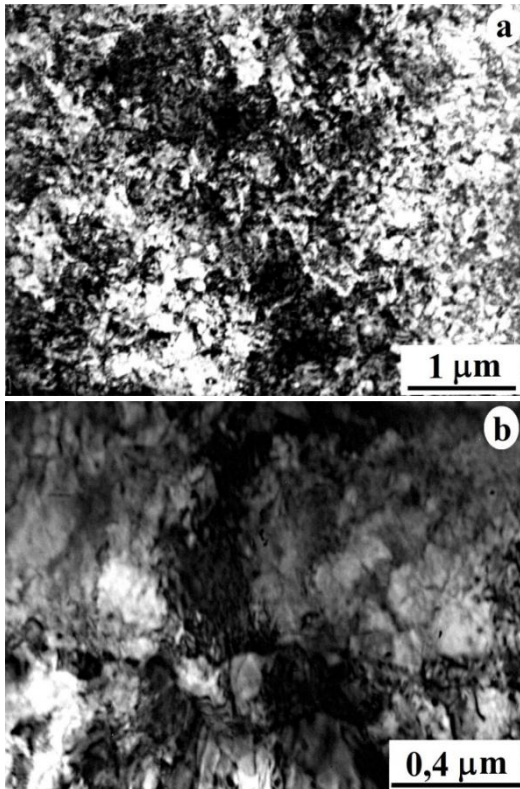


Fig. 2. TEM images of Zr1Nb alloy after following treatments: a – MT-1; b – MT-1+creep at 680 K ( $\sigma \approx 0.9\sigma_B$ )

It can be seen from the above figure and table that hydrogenation to 0.09 wt.% of samples of the deformed Zr1Nb alloy when tested under creep conditions at 300 K leads to a decrease in the strength characteristics

of the samples, but a plasticity does not change. In the process of creep at 680 K after hydrogenation, the strength characteristics and plasticity change slightly compared to the characteristics of the samples of the deformed alloy, however, it should be noted that the strength properties tend to increase.

Structural studies have shown that after combined rolling of the Zr1Nb alloy by a true strain value of  $\epsilon \sim 3.9$ , a nanostructure with a grain size of  $\sim 60$  nm is formed. The density of dislocations in the body of grains is  $\sim 3.4 \cdot 10^{10} \text{ cm}^{-2}$ . The main amount of dislocations is concentrated at the grain boundaries and triple junctions. The average size of misorientations caused by the boundaries is  $\sim 6^\circ$ . In this case, a high concentration of high-angle boundaries ( $8 \dots 30^\circ$ ), as well as dangling dislocation boundaries, is observed. The sharp inhomogeneity of the contrast in the electron microscope images indicates a high level of internal stresses and the presence of peak stresses at the junction of boundaries (Fig. 2,a).

The nanostructure created by IPD rolling turned out to be unstable to subsequent mechanical and thermal effects under creep conditions at 680 K (see Fig. 2,b). Most of the boundaries collapsed and in their place dislocation boundaries of the polygonal type were formed. The polygon sizes range from 50...150 nm. Extended boundaries with large, above 200, disorientation angles have been partially preserved.

When we studying the mechanisms of plastic flow of the nanostructured Zr1Nb alloy obtained using IPD, we showed [10–13] that plastic deformation occurs due to the transformation of the initial structure by the activation of recovery processes: dislocation climbing at the grain boundaries, the processes of generation and annihilation of dislocations at the boundaries, which leads to their scattering and is accompanied by stress relaxation. This process includes the destruction of the original structural configuration created as a result of rolling and the formation of a new structure that is less stressed and more resistant to subsequent deformation. The reason for the occurrence of the kinetic instability of the deformation structure is a changes in the geometry of plastic deformation and in the temperature-speed regime of deformation.

The reaction of the structure to annealing in a hydrogen atmosphere is nonuniform over the sample volume. In most places, recrystallization processes have taken place. This is the completed primary recrystallization, as well as collective recrystallization. However, polygonal boundaries are also visible. In other volumes, initial recovery processes in the crystalline and boundary phases with partial destruction of the deformation structure were revealed.

The size of new grains varies within a wide range of 0.08...0.5  $\mu\text{m}$ , but can reach  $\sim 2 \mu\text{m}$ . Such a sharp inhomogeneity of the recrystallized structure is called island inhomogeneity and can lead to changes in mechanical properties (Fig. 3,a,b). According to the state diagram of Zr-H [14], at a concentration of 0.09 wt.%, the amount of the  $\delta$ -phase in the  $\alpha$ -matrix is insignificant and, therefore, is not resolute by our methods.

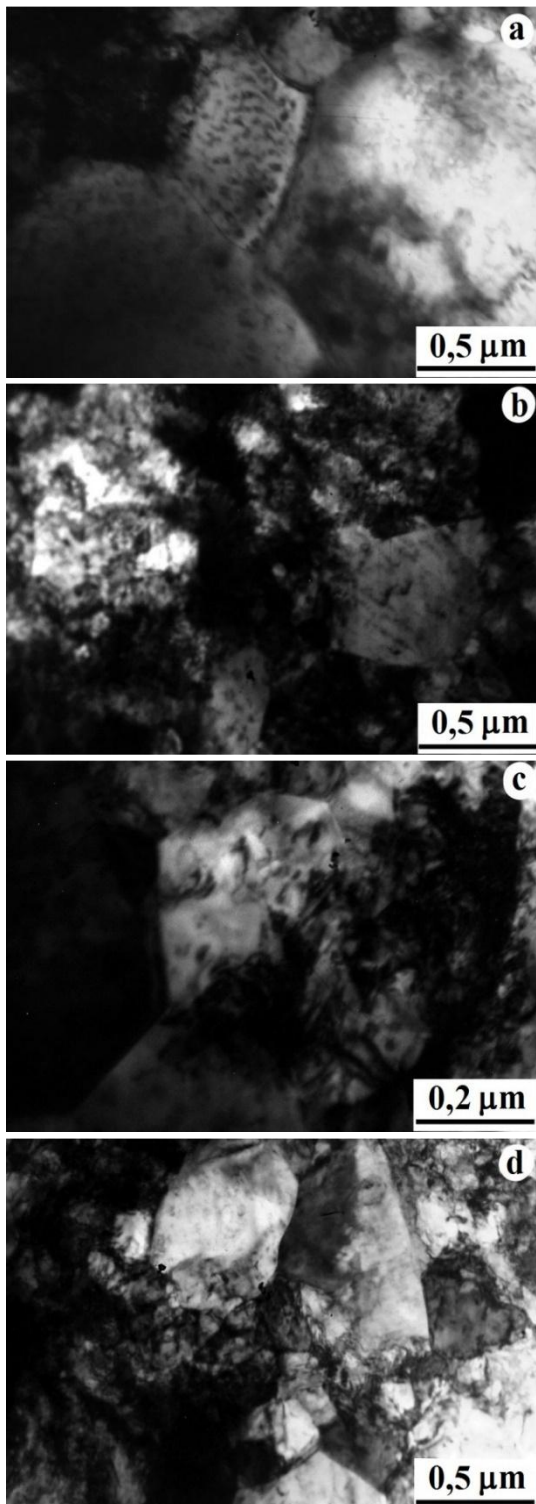


Fig. 3. TEM images of Zr1Nb alloy after following treatments: a, b – MT-2; c, d – MT-2+creep at 680 K ( $\sigma \approx 0.9\sigma_B$ )

The structure after creep at 680 K at the end of the uniform tensile region of the samples ( $\sigma \approx 0.9\sigma_B$ ) is inhomogeneous. In the recrystallized microregions, the processes characteristic of tension at elevated temperatures took place – the accumulation of dislocations with the formation of dislocation boundaries framing cells and fragments. In the volumes not affected by the processes of polygonization and recrystallization, intensive dynamic recrystallization took place ( $d = 0.05 \dots 1 \mu\text{m}$ ) (see Fig. 3,c,d).

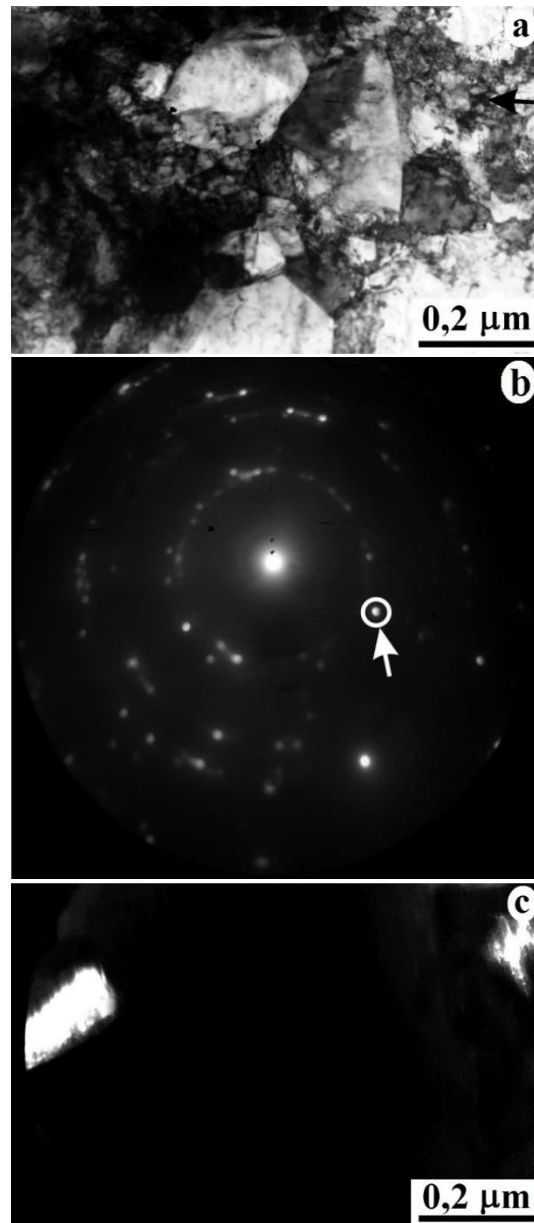


Fig. 4. TEM images of the Zr1Nb alloy after MT-2 and creep at 680 K ( $\sigma \approx 0.9\sigma_B$ ) having the precipitation of hydrides. Bright-field image of the structure (a); microdiffraction from an area of  $2 \mu\text{m}^2$  (b); dark-field image in reflection (311) (c); reflex and precipitate are shown by black and white arrows, respectively

The action of tensile loads during creep initiates the formation of zirconium hydrides – this is a  $\delta$ -phase with an fcc lattice and contains up to 55 at.% hydrogen. Individual sparsely spaced hydride precipitates, which do not interact with each other and are separated from the matrix by boundaries with a low degree of coherence, are short-range barriers for mobile dislocations (Fig. 4). The formation of such particles is possible in places of large structural discrepancy, which are powerful channel for hydrogen atoms and places of their excessive concentration.

The plastic flow in the region of macrolocalization is very inhomogeneous. Plastic deformation through the formation and displacement of new boundaries is carried out under conditions of dominant crystallographic anisotropy – a sharp rolling texture.

The recrystallization texture repeats the deformation texture, where the number of other admitted slip systems is sharply limited and the translational mode of dislocations is quickly exhausted.

Upon completion of primary recrystallization, when a critical concentration of structural discrepancy (triple junctions of boundaries) is reached, macrolocalization in the form of a “neck” is initiated. This means that the rate of plastic relaxation becomes less than the rate of plastic deformation. Usually, along with the formation of a dislocation and finely fragmented structure that is stable up to destruction, processes of dynamic recrystallization actively proceed, where microcracks are formed at the so-called critical junctions of grain boundaries. In our case, nuclei of secondary recrystallization are formed. Their size is less than 50 nm.

The growth of secondary grains is carried out under conditions of accelerated plastic flow and a gradual decrease in the structural elements of deformation. Finally, the formation of a new dissipative structure ends with the loss of stability of the entire system with the formation of delamination cracks at the junctions of new boundaries and destruction of the sample (Fig. 5).

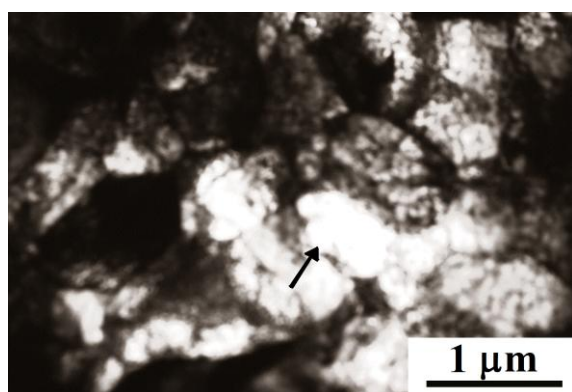


Fig. 5. TEM images in the area of pre-fracture of the Zr1Nb alloy after MT-2 during creep at 680 K. The arrow shows the initiation of discontinuities

An analysis of the obtained results shows that the observed features of the mechanical characteristics of the Zr1Nb alloy after the studied impacts are due to the characteristics of the obtained structures. Thus, a decrease in strength characteristics during creep tests at 300 K for samples of the Zr1Nb nanostructured alloy hydrogenated at 680 K for 5 h is a result, of a decrease in internal stresses. This is evidenced by the observed structural changes: polygonization, recrystallization, grain growth. However, the plasticity of the material did not change, which may be due to the strong inhomogeneity of the recrystallized structure.

At 680 K, the mechanical characteristics of the samples after rolling and after hydrogenation were almost the same. This may be a consequence, on the one hand, of the strong kinetic instability of the nanostructure obtained by rolling, as was shown earlier [10–13]. On the other hand, the structure recrystallized in the process of hydrogenation is inhomogeneous and, during creep, hydride precipitates with incoherent boundaries are formed in it, which are powerful obstacles in the way of dislocation glide. As a result,

there is a slight increase in the strength properties of hydrogenated samples.

## CONCLUSIONS

The regularities of creep, mechanical characteristics, and evolution of the structure of the nanocrystalline Zr1Nb alloy obtained by intensive plastic deformation and hydrogenated from a gaseous medium are studied.

It is shown that due to hydrogenation up to 0.09 wt.% and subsequent deformation under creep conditions, a small amount of hydrides is formed, which have little effect on the strength characteristics and plasticity of the Zr1Nb alloy.

The observed features of the mechanical characteristics of the hydrogenated nanostructured Zr1Nb alloy are mainly due to the past relaxation of internal stresses and the corresponding structural transformations during hydrogenation and subsequent creep.

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## **ВПЛИВ НАВОДНЮВАННЯ НА ПОВЗУЧИТЬ ТА ЕВОЛЮЦІЮ СТРУКТУРИ НАНОКРИСТАЛІЧНОГО СПЛАВУ Zr1Nb**

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Досліджено закономірності повзучості, механічні характеристики та еволюцію структури нанокристалічного сплаву Zr1Nb, отриманого шляхом інтенсивної пластичної деформації та насиченого воднем з газового середовища. Показано, що внаслідок деформації в умовах повзучості в структурі сплаву Zr1Nb утворюється невелика кількість гідридів цирконію, що мало впливає на його міцнісні властивості та пластичність. Спостережувані особливості характеристик повзучості зумовлені в основному релаксацією внутрішніх напружень і відповідними структурними перетвореннями під час наводнювання та подальшої деформації.