Research of Hydrogen ChargInG in Zirconium Alloy by Thermo-desorption Method

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Abstract – The hydrogen thermo-stimulated yield from zirconium alloy charged by hydrogen depending on degree of lengthening strain is investigated. Samples of zirconium alloy were exposed to a tension with specific elongation of 2.5 %, 5.0 % and 10.0 %, and then electrolytic charged with hydrogen at current density J=0,5 A/sm^2 during 4 hours, and vice versa they were first charged with hydrogen and then exposed to strains. Strains and hydrogen charging of samples give the formation of hydrogen traps with different binding energies. Binding energies and quantity of hydrogen entrapped in traps depend both on specific elongations at strain, and an operating sequence "strain-charging". Quantities of hydrogen binding energies in traps are estimated. Types of traps are identified.

1. Introduction

Zirconium alloys owing to small section absorption of thermal neutrons, high stability corrosion, a good mechanical properties and ease of processing are the basic constructional materials for systems of nuclear power reactors [1]. One of the important requirements to materials of a fissile region of reactors is low sorption of hydrogen. Hydrogenation results in decrease of a plasticity and crack resistance of alloys and formation of brittleness hydrides in zones of a stress concentration can become the failure of destruction of items due to formation and grows hydride flaws on the mechanism of delayed destruction at temperatures of maintenance. Zirconium alloys are actively absorption hydrogen already at 300 ºC, forming a solid solution and hydrides ZrH and ZrH_2 [2]. Therefore the interconnection between elastic performances of zirconium alloys of and behaviour of hydrogen saturating them represents fundamental interest both from the point of view of reactor safety, and from the point of view of opportunity of zirconium mechanical characteristics.

The purpose of this work was to study of hydrogen regularities the accumulation depending on strain of zirconium alloy Э125 (Zr − 2,5 % Nb), which use in hi-tech units of the atomic power station.

2. Experimental details

Three series samples of zirconium alloy Э125 by thermo-desorption method (TDM) was researched:

1. Initial and exposed to strains (tensile) with specific elongate $\Delta\ell/\ell$ = 2.5; 5.0 and 10.0 %.
2. Initial and exposed to strains with the specific elongation $\Delta\ell/\ell$ = 2.5; 5.0 and 10.0 %, and then electrolytic charged with hydrogen at current density J=0,5 A/sm^2 during 4 hours.
3. In the beginning were charged with hydrogen, and then were exposed to strains; parameters of saturation and tensile, as in item 2.

The initial samples with dimensions 30×3×3 mm mechanically polished and annealing at pressure 10^{-4} Pa and temperature 550 °C during 60 mines with the subsequent cooling without a deterioration of vacuum. Hydrogen charging was made in the electrolytic cell at using samples as cathodes. Electrolyte – H_2SO_4 molar concentration at temperature 20 °C.

Installation for TDM research was described in [3]. The block of a programmed heating allows a linear heating from 20 up to 1100 ºC with velocity from 0,1 up to 5 degree/sec. The chamber of heating samples is mating through the lock with monopole mass-spectrometer MX-7304. Pressure in measuring cell of the mass-spectrometer is not higher 10^{-5} Pa.

For an estimation of a binding energy of hydrogen in traps we used the method which bases on calibrations dependence of the desorption activations energy E_d from temperature $T_{max,i}$ at which take a place i-maximum in dependence of hydrogen yield on temperature [4]. For comparison of the content hydrogen in different samples the temperature dependences of hydrogen yield from temperatures (HYT) were integrated on the complete time of a heating. The presented HYT were received at velocity heating of 1 degree/sec.

3. Results and discussion

Figs. 1−3 shows dependences of intensities thermo-enhanced hydrogen yield from temperature. Fig. 4 show dependences of an integrated hydrogen yield strain and charged samples.

Comparison of curves in Figs. 1−3 shows, that strain and charging zirconium alloy Э125 samples with hydrogen, bring to complicating of HYT − salient feature (peaks, steps, bends) are appear. By arrows in Figs. 1−3 shows maximums of temperature T_{max}, corresponding to these appearances. From Fig. 1 show, what even charging of an initial (undeformed) sample by hydrogen is brings to increase intensity of hydrogen yield and complication of HYT. That salient features are observed on all curves HYT, but them

T_{max} differ, though some from them (for example, at T_{max} = 515 ºC) are observed on all samples, undergone to hydrogen charging.

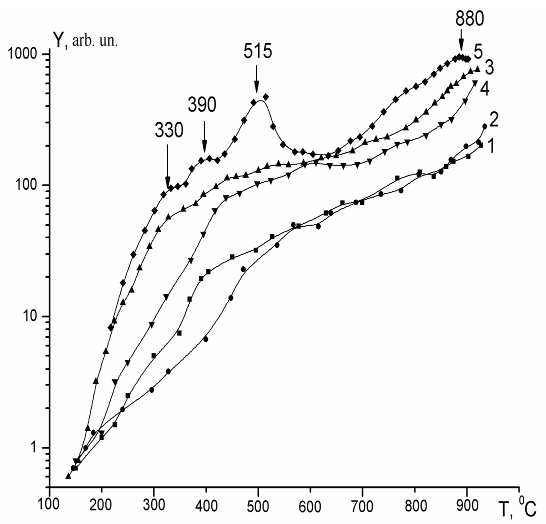

Fig. 1. Temperature dependences of hydrogen yield from samples zirconium alloy Э125: 1) undeformed sample; with specific elongation Δℓ/ℓ, %: 2) 2.5; 3) 5.0; 4) 10.0; 5) undeformed and hydrogen charged sample

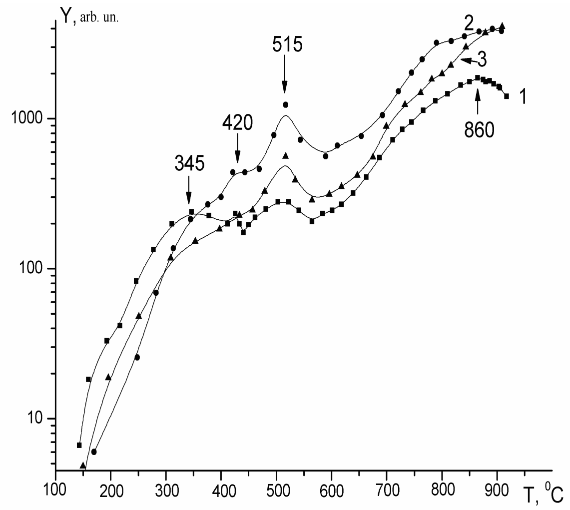

Fig. 2. Temperature dependences of hydrogen yield from samples zirconium alloy Э125 exposed to strains and then electrolytic charged with hydrogen 1 Δℓ/ℓ = 2.5 %; 2) Δℓ/ℓ = 5.0 %; 3) Δℓ/ℓ = 10.0 %

Let's designate type the sample "F+H" if the sequence of operations corresponds strain and then hydrogen charging; "H+F" − hydrogen charging and then strain samples; "F" − strained, but not hydrogen charged samples. Let's choose characteristic areas of temperatures in which regularities of HYT curves are observed. To these areas corresponds the specific type of hydrogen traps, which we shall numbers again (further shall identification types of traps). Therefore, the information about regularities of HYT can be presented as table 1. From tab.1 you can see, that binding energy in the studied temperature ranges differ in the 100-th shares of eV and therefore it is possible to believe, that in the given range we deal with one type of traps.

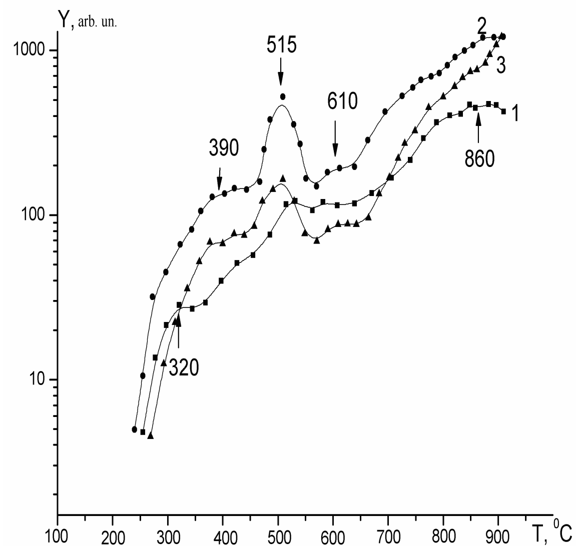

Fig. 3. Temperature dependences of hydrogen yield from samples zirconium alloy Э125 electrolytic charged with hydrogen and then exposed to strains 1) Δℓ/ℓ = 2.5 %; 2) Δℓ/ℓ = 5.0 %; 3) Δℓ/ℓ = 10.0 %

Table 1. The type of traps (1–5), corresponding to them of temperature activation (T_{max}), binding energy (E_b) atoms hydrogen in traps and identification types of traps

Types of traps	T_{max}, ºC	E_b eV/atom	Identification types of traps
1	320…345	1,70...1,77	dislocations
2	390…420	1,90...1,98	
3	515	2,25	
4	610	2,53	micro pores and cracks
5	860…880	3,24...3,30	

The relative quantity of the hydrogen which captured on traps, is defined by the order of operations "strain-charging". It is follows as from comparison intensities of different regions the HYT curves (corresponding to traps 1–5) in Figs. 1−3 so integrated of hydrogen yield in Fig. 4.

The comparison of curves in Fig. 4 shows, that an integrated of hydrogen yield:

1) raises in some times from the deformed samples even in case them did not hydrogen charge neither up to, nor after deformation;
2) from samples deformed and then electrolytic hydrogen charged is essentially above, than in other cases;

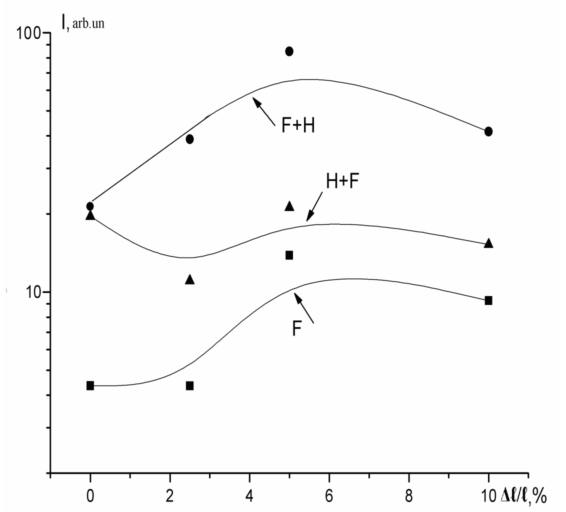

Fig. 4. Dependences the integrated hydrogen yield from degree of deformation

3) in cases when samples were electrolytic hydrogen charged, the size of deformation influences weak an integrated of hydrogen yield.

The maximal integrated of hydrogen yield is observed at 5 % deformations. At 10 % in the researched range of temperatures the yield is lower, than at 5 % deformation. The maximum thermo-enhanced hydrogen yield from zirconium alloy takes a place above 1000 ºC and behaviour character the curves HYT near 1000 ºC shows, that this maximum at 10 % deformation is higher than in any cases. Really, near 1000 ºC intensity of curves HYT from samples with $\Delta\ell/\ell$ = 10 % (the curve 3 in Figs. 2 and 3) grows faster than others so the curve 3 is crossed with a curve 2. That is at the big deformation degree the hydrogen grasps and collects by traps with the big energy of binding for which $T_{max} > 1000$ °C and $E_b \geq 3$ eV. These traps we identificate as strong binding type 4–5 and 1–3 with weak binding (tab. 1).

Let's receive numerical estimations of hydrogen redistribution at deformation between traps with weak and strong binding. In case of 10 % deformations we shall divide intensity of curve 5 Fig. 1, and also curve 3 Fig. 2 and Fig. 3 in the points corresponding to the maximal temperature (~1000 ºC) on intensity of the same curves in the points corresponding the first and third types of salient features (that is corresponding to temperatures 330 and 515 ºC).

From results of the numerical estimations presented in tab. 2 you can see, that the relative hydrogen yield from traps with strong binding at deformation increases more than 2 times in comparison with traps of type 1 and more than 3 times in comparison with traps of type 3.

Table 2. Comparison of relative hydrogen yield from traps with strong and weak binding

Type of traps	T_{max} °C	Type of sample: Initial, charging of hydrogen	F+H	H+F
		Y, arb. un.		
5	880	943	4099	1210
1	330	57	130	35
3	515	473	562	164
Ratio	Y_{880}/Y_{330}	15,5	31,5	34,5
	Y_{880}/Y_{515}	1,99	7,3	7,4

All these regularities allow traps of type 1–4 identify as dislocations (with their various modifications) and grain interface; traps of type 5 and more height-energy as micro pores and cracks. Such interpretation is obvious at the given ordering of experiment, because at tensile of samples a dislocation and grain interface give rice to pores and cracks.

4. Conclusion

It is established, that deformations zirconium alloy results in the formation traps with different energy of hydrogen binding. The primary type of traps depends on a degree deformation. Energy binding and quantity of the hydrogen captured in traps specific elongates of operations "strain-charging". The energy binding of hydrogen in observable types of traps are appreciated. The most probable identification of traps is defined.

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