Technical sciences

UDC 539.16.04

THE INVESTIGATION OF HYDROGEN ACCUMULATION IN ZIRCONIUM ALLOY BY THERMOSTIMULATED GAS EVOLUTION METHOD

N.N. Nikitenkov, Y.I. Tyrin, I.P. Chernov, A.V. Skirnevsky, G.V. Garanin, A.M. Lider, Y.P. Cherdantsev

Tomsk Polytechnic University
E-mail: nikitenkov@fnsm.tpu.edu.ru

Thermostimulated gas evolution from zirconium alloy saturated by hydrogen E-125 versus deformation degree has been studied. Samples of zirconium were subjected to straining with relative lengthening 2,5; 5,0 and 10,0 %, then they were saturated with hydrogen by electrolyte method at current density 0,5 A/sm² during 4 hours. Or vice versa, they were first saturated with hydrogen being subjected to deformation afterwards. The deformation of alloy samples results in trap formation with different energies of hydrogen bond. In this case both bond energy and hydrogen quantity caught in traps depends on both deformation size and succession of «deformation-saturation» actions. The values of hydrogen bond energies in traps are estimated. Types of traps are defined.

Introduction

Zirconium alloys are main constructional material for the elements of active zone and fuel systems of atomic reactors owing to small section of absorption of thermal neutron, high corrosion resistance, good mechanical properties and easy treatment [1]. One of the important demands of active zone materials is low hydrogen absorption. Saturation with hydrogen results in decrease of alloy plasticity and crack resistance, brittle hydrides in the range of stress concentration can become a cause of product destruction because of formation and growth of hydride cracks according to mechanism of delayed destruction at the temperature of operation.

Zirconium alloys absorb hydrogen actively even at 300 °C forming solid solution and hydrides ZrH and ZrH_2 [2]. Therefore interdependence of elastic characteristics of zirconium alloys and behavior of saturating hydrogen is of fundamental interest both from the point of view of reactor facility safety and from the point of view of possibility to operate the mechanical properties of zirconium.

The purpose of the given work is to examine regularities of hydrogen saturation depending on deformation degree of binary zirconium alloy samples of E-125 type (Zr–2,5 % Nb) used in some high technological APP units.

Methods of experiment

By means of thermostimulated gas evolution method (TSGE) 3 groups of binary zirconium alloy samples of E-125 have been investigated:

1. Initial and deformed (strained) samples with relative lengthening $\Delta\ell/\ell$=2,5; 5,0 и 10,0 %.
2. Initial and deformed at the beginning with the same relative lengthening, but then saturated with hydrogen by electrolyte technique with current density J=0,5 А/см² during 4 hours.
3. First saturated with hydrogen, then deformed; the parameters of saturation and straining are the same in point 2.

Initial samples of 30×3×3 mm size were polished mechanically and annealed at pressure 10^{-4} Pa and temperature 550 °C during 60 min with subsequent cooling in furnace without vacuum deterioration. Hydrogen saturation was carried out in electrolytic cell using samples as cathodes. Electrolyte – H_2SO_4 of molar concentration at temperature 20 °C. To strain the samples experimental equipment Com-Ten DFM 5000 was used.

The equipment to investigate TSGE is described in the works [3, 4]. Unit of programmed heating allows for linear heating samples from 20 to 1100 °C with velocity from 0,1 to 5 degree/sec. Heating chamber is connected with single mass-spectrometer MX-7304 through sluice. Such a construction provides quick change of investigated samples as well as continuous recording of intensivities produced at gas heating of mass from 1 to 250 а.е.м. In the measuring cell of the mass-spectrometer vacuum is not worse than 10^{-5} Pa. Final pumping out was made by ion pumps. The relative error of intensivity measurement of the mass lines is not more than 5 %. Before the experiment repeated heating of vacuum cell without sample showed that intensivity of H_2 hydrogen evolution increases in comparison with vacuum level maximum 5...6 times at temperature higher 800 °C. When heating vacuum cell with the sample gas evolution intensivity increases in comparison with vacuum level up to four-fold (fig. 1–3).

Therefore in the figures below one can see intensivity dependences of thermostimulated H_2 hydrogen evolution from the samples of zirconium alloy E-125 without subtraction of heater hum of the vacuum cell.

To estimate hydrogen bond energy in the traps a method based on calibrating lines of desorption activation energy dependency E_d on temperature $T_{max,i}$ was applied, at which i-maximum of hydrogen evaluation on temperature and velocity of heating was observed [5]. Using the given dependences and taking into account small differences between hydrogen atom bond energy in the sample E_b and desorption activation energy E_d one can evidently use the dependences to estimate E_b. To compare hydrogen content in different samples the temperature dependences of hydrogen evaluation on TSGE temperature (spectra) were integrated according to total time of heating. The spectra TSGE presented below were obtained at heating velocity 1 degree/sec.

Results and discussion

In fig. 1–3 the intensivity dependences of thermostimulated hydrogen evolution from the samples on temperature are shown.

In fig. 4 the dependences of integrated hydrogen evolution on degree of deformation and hydrogen saturation are presented. Integration was made by means of integration module from applied program package OriginPro 7.0 (OriginLab Corporation).

The comparison of the curves in fig. 1–3 shows that deformations and hydrogen saturation of zirconium samples E-125 result in complication of type of TSGE temperature dependence, there appearing some peculiarities (peaks, steps, discontinuities). The temperature maximums $T_{max,i}$ corresponding the peculiarities are shown in fig. 1–3 by arrows. It should be noted that specific peculiarities are observed in all TSGE spectra, but their T_{max} are different, though some of them (for example, at T_{max}=515 °C) are observed in all samples subjected to hydrogen saturation.

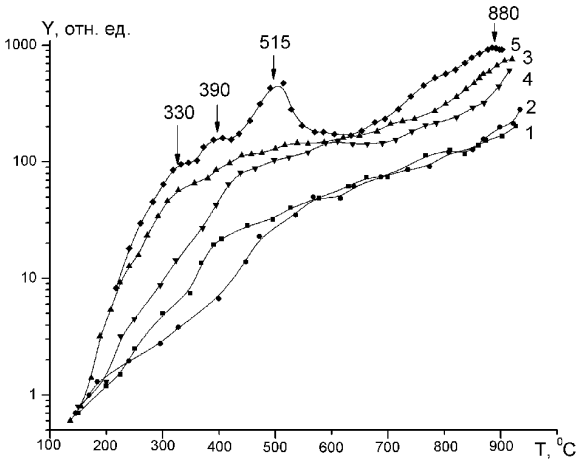

Fig. 1. *The temperature dependences of TSGE intensivity from zirconium alloy samples E-125: 1) undistorted sample and that subjected to straining with relative lengthening $\Delta\ell/\ell$, %: 2) 2,5, 3) 5,0, 4) 10,0; 5) undistorted, hydrogen saturated sample*

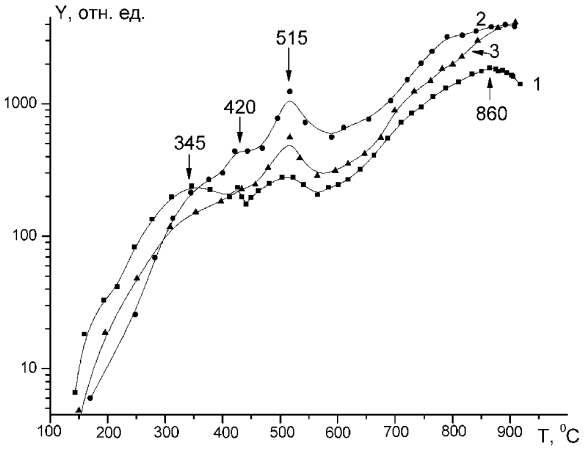

Fig. 2. *The temperature dependences of TSGE intensivity from zirconium alloy samples E-125, first subjected to deformation and then hydrogen saturated by electrolyte $\Delta\ell/\ell$, %: 1) 2,5, 2) 5,0, 3) 10,0*

It should be pointed out that specific peculiarities are observed on all TSGE curves, but their T_{max} are different, though some of them (for example, at T_{max}=515 °C) are observed in all samples subjected to hydrogen saturation.

It is known that peculiarities mentioned are connected with hydrogen evolution from traps with definite desorption activation energy E_d, the E_d values being uniquely connected with T_{max} [5]. To analyze the peculiarities of TSGE spectra let us take some abbreviations and assumptions. Denote the type of sample «F+H» if the sequence of operations corresponds to first its straining, then hydrogen saturation, and, on the contrary, «H+F» denotes first hydrogen saturation then sample straining, «F» denotes deformed, but not saturated samples. Let us point out the characteristic temperature regions where spectra peculiarities are situated. Evidently, each of the regions corresponds to definite type of hydrogen traps which are first numbered (hereinafter arguments in favour of concrete defects responsible for each of the type of traps will be adduced)

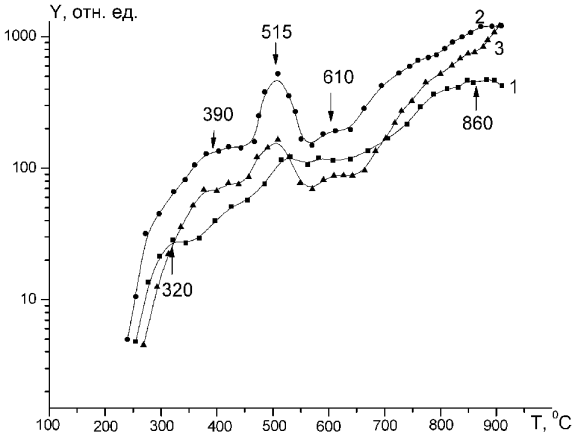

Fig. 3. *The temperature dependences of TSGE intensivity from zirconium alloy samples E-125, first hydrogen saturated by electrolyte and then subjected to deformation, $\Delta\ell/\ell$, %: 1) 2,5, 2) 5,0; 3) 10,0 %*

Thus, the information on TSGE peculiarities can be presented in the tables 1 and 2.

Table 1. *Types of traps (1–5), activation temperatures corresponding to them T_{max}, desorption activation energy (E_d) and hydrogen atom bond energy in traps (E_b)*

Type of trap	T_{max}, °C	E_d, kkal/mole	E_b, eV/atom
1	320...345	39,0...40,7	1,70...1,77
2	390...420	43,7...45,7	1,90...1,98
3	515	52	2,25
4	610	58,2	2,53
5	860...880	74,6...76,1	3,24...3,30

From table. 1 it is obvious that in the set up temperature range the bond corresponding to energy vary in hundredth parts of eV, therefore it is supposed that we deal with one of the types of trap in the given range.

Table 2. *Classification of TSGE spectra peculiarities fig. 1–3*

Type of samples	$\Delta\ell/\ell$, %	Presence of traps of the given type («+» – present, «–» – absent)				
		1	2	3	4	5
Initial	0	+	+	+	–	+
F+H	2,5	+	–	+	–	+
F+H	5,0	+	–	+	–	–
F+H	10,0	–	+	+	–	–
H+F	2,5	+	–	+	+	+
H+F	5,0	–	+	+	+	–
H+F	10,0	–	+	+	+	–

From table 2 it is obvious that the presence of each type of trap in samples depends on deformation size and sequence of deformation and saturation. Relative quantity of hydrogen caught in the traps is defined by the order of deformation and saturation operations. One can see it both from comparison of intensivity of different regions. It is seen both from the comparison of intensivity of different parts of TSGE spectra (corresponding traps 1–5) in fig. 1–3 and from that of total values of the absorbed hydrogen (fig. 4).

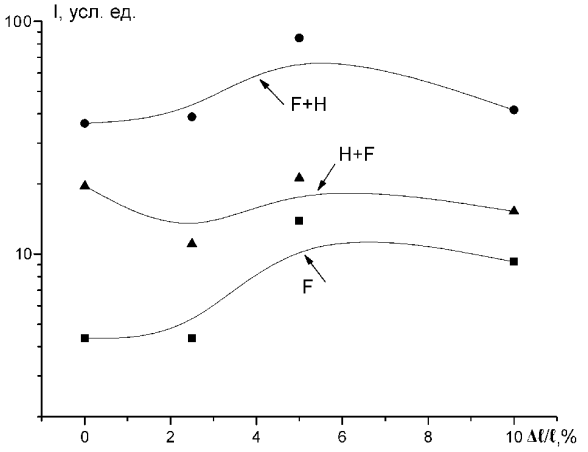

Fig. 4. *The dependences of integral evolution of hydrogen on the degree of deformation (The value of error along both axes is not more than linear point size*

The most quantity of hydrogen is trapped at «F+H» sequence of operation.

The comparison of the curves presented in fig. 4 shows that integral evolution of heat:

1. increases some times from deformed samples even in the case if they are not saturated with hydrogen neither before nor after deformation;
2. is significantly higher from samples first deformed, then saturated than in the other cases.
3. in the case when samples first saturated with hydrogen the deformation value slightly influences the integral evolution.

The maximum integral evolution of hydrogen is observed at 5 %-deformation, at 10 %-deformation the evolution in the given temperature range being lower than at that of 5 %. It does not mean, however, that relatively small deformations (≤5 %) provide hydrogen accumulation, but at large deformations (≥10 %) hydrogen is distilled from sample. The point is that maximum heat evolution of hydrogen from zirconium alloy is higher 1000 °C and TSGE spectra pattern behaviour near 1000 °C shows that this maximum at 10 % deformation is essentially higher than in any other cases. In fact, near 1000 °C intensivity of TSGE spectrum from samples from $\Delta\ell/\ell$=10 % (curve 3 in fig. 2, 3) increases distinctly quicker than the others, so that curve 3 crosses curve 2. I.e. at more degree of deformation hydrogen is captured and mostly accumulated by traps with large bond energy for which T_{max}>1000 °C, a E_b≥3 eV. Let us name the traps as trap with strong bond, but traps of type 1–4 (table 1) that with weak bond.

Obtain numerical evaluation of hydrogen redistribution between traps with weak and strong bonds at deformation. For this purpose in the case of 10 % deformation divide the spectrum intensivity 5 in fig. 1, as well as that of spectra 3 in fig. 2 and 3 in the points corresponding maximum temperature (~1000 °C) by intensivity of the same spectra in the points corresponding the first and third types of peculiarities (i.e. temperature 330 и 515 °C). From the results of numerical evaluation presented in table 3 it is seen that relative evolution of hydrogen from the traps with strong bond at deformation increases more than 2 times in comparison with the traps of type 1 and more than 3 times in comparison with the traps of type 3.

Table 3. *Comparison of relative hydrogen evolution from the traps with strong and weak bonds*

Types of traps	T_{max} °C	Types of samples		
		Initial, saturated with hydrogen	F+H	H+F
		Y, rel. units		
5	880	943	4099	1210
1	330	57	130	35
3	515	473	562	164
Relations	Y_{980}/Y_{430}	15,5	31,5	34,5
	Y_{980}/Y_{615}	1,99	7,3	7,4

The regularities described above permit to define the traps of 1–4 types as dislocation (with their different modifications) and grain boundary, but the traps of type 5 and

more highly energetic ones (not observed in our experiment) are defined as microvoids and cracks. On the whole, such interpretation in the given experiment is obvious because when straining the samples it is just dislocations and grain boundaries that give rise to pores and cracks.

Conclusion

It was stated that deformations of zirconium alloy E-125 result in trap formation with different hydrogen bond energies. The primary type of traps depends on deformation degree. Bond energy and quantity of hydrogen captured in the traps depend on value of deformation as well as on sequence of deformation and saturation operations. The values of bond hydrogen energies are estimated in the traps under study, the most probable identification of traps is given.

The work is done at the International scientific technical centre support, grant № 2864.

Literature

1. Duglas D. Material study of zirconium. – Moscow: Atomizdat, 1975. – 360 p.
2. Nikulin S.A., Rozhnov A.B., Babukin A.V. a. o. The structure and resistance to distruction of zirconium alloys for atomic power engineering // Material science and thermal treatment of metals. – 2005. – № 5. – P. 8–17.
3. Turin Y.I., Chernov Y.I., Krening M., Baumbakh Ch. Radioactively stimulated evolution of hydrogen from metals. – Tomsk: TSU, 2000. – 263 p.
4. Turin Y.I., Chernov Y.I., Krening M., Baumbakh Ch. Excitement of hydrogen subsystem in metals and alloys by ion radiation // Proceedings of Tomsk Polytechnic University. – 2000. – V. 303. – № 3. – P. 51–61.
5. Woodraf D., Delchar T. Modern methods of surface investigation. – Moscow: Mir, 1989. – 564 p.

UDC 537.9:539.12

DIELECTRIC RESPONSE FUNCTION PdH_x SYSTEM

Y.M. Koroteev*, O.V. Girmanova, I.P. Chernov

*Resistance physics and material science institute of RAS, Tomsk
Tomsk polytechnic university
E-mail: yury_koroteev@list.ru

The calculations of electron structure of pure Pd and PdH_x (x=1,2,3) system have been made ab initio in the range of local density approximation. Total energy of PdH_x system has been calculated for the cases of different coordination of hydrogen atom (oct-and tetrahedral), the conclusion on their most probable location in metal lattice has been made. In the approximation of constant matrix element the imaginary part of permittivity constant function $\varepsilon_2(\omega)$ has been calculated. It was stated that dissolution of hydrogen in palladium increases values of the function $\varepsilon_2(\omega)$ in the investigated range of energies from 2 to 24 eV. Therefore in the case of radiation impact on PdH_x system one can expect intensive excitement of the crystal electron subsystem, and, hence, decrease of potential barriers for hydrogen atom movement.

Introduction

A unique ability of palladium to dissolve large quantity of hydrogen was discovered by T. Graham as early as in 1886. Hydrogen dissolution changes the physical properties of palladium considerably [1, 2]: increases lattice parameter, decreases conductivity and magnetizability, raises hardness and strength, decreases plasticity, results in embrittlement. PdH_x system is diamagnetic and possesses superconductivity; whereas pure Pd is paramagnetic and as it is known does not exhibit superconductivity [3]. It is evidently that these changes of palladium properties are connected with modification of its atomic and electron structure when dissolving hydrogen in it.

Dissolving hydrogen palladium retains its type of crystal lattice. At small concentration of hydrogen ($x<0,03$) the so called α-phase PdH_x is formed. At high concentration of hydrogen ($x>0,6$) the solution is changed into β-phase with peculiar for the phase change of the first type the uneven change of lattice constant. Dissolving in palladium hydrogen atoms occupy in interstitial spaces of its face-centred cubic (FCC) crystal lattice. FCC lattice is known to have two types of interstitial spaces: tetrahedral and octahedral. Based on the data of neutron diffraction [4–6], it was inferred that hydrogen atoms occupy octahedral interstitial spaces in FCC lattice of palladium forming PdH monohydride with NaCl structure. However, there are someata on concentration and temperature dependencies of electrical resistance of PdH monohydride as well as neutron structure investigations [3, 6], indicating the transformation of hydrogen atoms from oct- into tetrahedral type at temperature of order 50 K.

During recent experiments information about hydrogen behavior in palladium lattice exposed to the action of ionized radiation has been obtained. So, the experimental data on radioactive stimulated hydrogen migration and desorption from palladium including