REGULARITIES OF RADIATION AND HETEROGENEOUS PROCESSES IN CONTACT OF Zr AND Zr1%Nb ALLOY WITH WATER

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Influence of radiation in the processes of hydrogen accumulation and zirconium oxidation as a result of heterogeneous processes in contact of zirconium and a Zr1%Nb alloy with water vapors is investigated. The contribution of radiation processes in these contacts on radiolysis and thermic radiolysis processes of water decomposition is revealed. It is established that radiation processes in contact of zirconium materials with water cause acceleration of molecular hydrogen accumulation processes, as a result of protective oxide film formation on a surface, and destructive oxidation.

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INTRODUCTION

Study of the physical and chemical processes proceeding in contact of metal constructional materials of nuclear reactors with water at simultaneous influence of temperature and radiation represents great interest when solving problems of materials science and safety of operation of nuclear power plants. Features of these processes are related to that they can come to the end on the one hand by corrosion of constructional materials, and on the other hand by the accumulation of explosive gas products in the environment [1–10, 12,15].

For identification of a safe operating mode and an assessment of consequences of accidents with damage of a core of nuclear reactors, it is represented great interest to establish regularities of molecular hydrogen accumulation at impact of radiation and temperature on the coolant in contact with construction metal materials in normal and accident operation mode [7–9, 14].

The analysis of literary materials shows that in the water-cooled nuclear reactors, a radiolysis processes in water at a liquid and steam state are considered as a source of molecular hydrogen. In these works, radiolytic processes of hydrogen accumulation in reactors were characterized by a yield of molecular hydrogen which is allocated at a homogeneous radiolysis of water, and influence of radiation and radiation-thermal processes in contact of constructional materials with water on processes of H_2 accumulation wasn't considered at all [6, 8].

In this work a regularities of radiation, radiation-thermal and thermal processes of molecular hydrogen accumulation in contact of nuclear grade zirconium and a Zr1%Nb alloy with water are studied.

EXPERIMENTAL PART

Samples subjected to preliminary radiative effects by gamma rays ($\dot{D}$ = 7.17 Gy/s) at various times (τ = 5…500 h), then dried up, weighed and transferred to special ampoules for test of radiation and catalytic activity in processes of radiolytic decomposition of water.

Tests were carried out in static conditions in special quartz ampoules with the volume of 0.25…0.30 cm^3. It was taken nuclear grade zirconium with purity of 99%, a zirconium alloy with 1% of Nb in the form of a thin tape and bidistilled water as objects of research. The calculation of contact surface area for samples was based on their geometrical sizes and was equal to 34.6 g/cm^2. For exception of a contribution of organic pollution on a surface to process of H_2 accumulation, samples cleared previously by organic solvents – ethyl alcohol, acetone, and then washed out by the distilled water. Then samples dried up at a temperature of 300…320 K in the environment of inert gas of argon. The dried-up samples were weighed with an accuracy of $\pm 5 \cdot 10^{-3}$ g and transferred to quartz ampoules. Ampoules with samples were vacuumized to $P \approx 10^{-3}$ Pa, at first at T = 300 K and then at T = 673 K. The necessary amount of water was entered into an ampoule with samples by condensation of water vapors from the graduated volume of vacuum-absorbing device. Radiation and radiation-thermal processes in the ampoules with samples soldered by this way were carried out on an isotope source of γ-radiation ^{60}Co. Thermal and radiation-thermal processes were carried out in the range of T = 473…1073 K, and in this case the contact of water vapors with Zr takes place. Dosimetry of a source was carried out by chemical dosimeters – ferrosulfate, cyclohexane and methane. Recalculation of a dose in the studied system was made by comparison of electronic density [13].

Gas products of processes were transferred to the special graduated volumes and analyzed by method of a gas chromatography ("Agilent-7890"). It was observed also O_2 at radiolytic process at T = 300 K and mainly H_2 at thermic radiolysis as a part of gas products.

RESULTS AND THEIR DISCUSSIONS

For the purpose of identification of metal materials influence on water radiolysis the kinetics of accumulation of hydrogen at radiolytic decomposition of water in the presence of nuclear grade zirconium at 296 K is investigated. Radiation-chemical yields of H_2 thus made 0.54 and 0.44 molec./100 eV. The observed gain of values of a radiation-chemical yield of molecular hydrogen at water radiolysis in the presence of metal materials in comparison with an yield of a pure water radiolysis, can be explained with a contribution of emitted electrons from metal at influence of γ-quanta, and creation of the additional active centers for water decomposition on a surface of metals. Gain of rates of a water radiolysis at superficial space of metal zirconium

and a Zr1%Nb alloy makes $\Delta W = 3.44 \cdot 10^{12}$ and $5 \cdot 10^{12}$ molec./(cm^2·s), respectively.

In operating conditions of nuclear reactors a metal constructional materials are exposed to simultaneous influence of temperature and radiation in contact with coolants. Therefore detection of regularities of radiation and thermal superficial processes of H_2 formation in contact of water with metal materials represents great interest.

The kinetics of accumulation of molecular hydrogen was for this purpose investigated at radiation-thermal and thermal processes in contact of Zr and Zr1%Nb alloy with water and on the basis of initial linear sites of experimental kinetic curves, the values of rates of these processes – $W_{RT}(H_2)$ and $W_T(H_2)$ respectively are defined.

Rate of a radiation component $W_R(H_2)$ of radiation-thermal process of hydrogen accumulation, can be determined from a difference of rates of radiation-thermal and thermal processes:

$$W_R(H_2) = W_{RT}(H_2) - W_T(H_2).$$

It was studied by a weight method the kinetics of formation of an oxide phase on a surface of the studied materials as a result of radiation-thermal and thermal processes in their contact with water (Fig. 1). Experimental results show that formation of an oxide film and accumulation of H_2 as a result of these processes can be explained by the next equation:

$$Zr + 2H_2O \xrightarrow{T} ZrO_2 + 2H_2 \quad . \qquad (1)$$

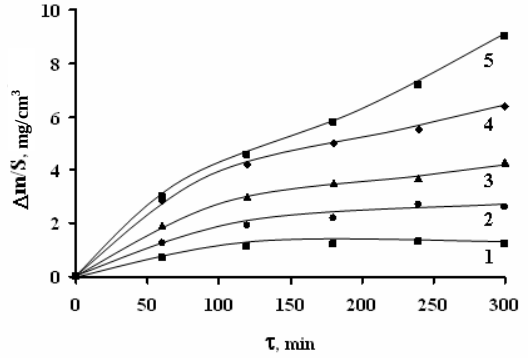

Fig. 1. Kinetics of oxidation of a Zr1%Nb alloy at radiation-thermal ($\dot{D}$ = 7.16 Gy/s): 1 – T = 473 K, 3 – T = 873 K, 5 – T = 1073 K; thermal processes: 2 – T = 873 K, 4 – T = 1073 K in contact with water (ρ_{H_2O} = 5 mg/cm^3)

It is established that the contribution of thermal processes in accumulation of molecular hydrogen and process of metals oxidation in contact of the cleared surface of zirconium metal and a Zr1%Nb alloy with water, becomes notable with T = 473 K and increases with growth of temperature. At T ≥ 1073 K the radiation component of radiation-thermal process in comparison with thermal, becomes imperceptible – $W_T(H_2) >> W_R(H_2)$. It is conditionally possible to allocate two areas [19] in kinetic curves of accumulation of molecular hydrogen and oxidation of zirconium materials at radiation-thermal processes (Fig. 2):

I – the area corresponding to accumulation of H_2 as a result of heterogeneous processes with formation of a protective oxide phase on a surface of zirconium materials;

II – area accumulation of H_2 as a result of destructive oxidation of materials which happens at T > 873 K.

The first area of oxidation of zirconium materials in contact with water comes to the end by formation of a black oxide film with deficiency of oxygen ($ZrO_{1.95}$) [3, 9]. It protects zirconium from further oxidation. Completion of a protective oxide layer formation on a zirconium surface is shown in the form of saturation area in kinetic curves of oxidation. At a long time of contact with water, in conditions under the influence of radiation and temperature in an oxide film and in Zr-ZrO_2 system, defective states and pores collect in a large number which lead to formation of destructive oxidation area of zirconium materials [18]. Comparison of kinetic curves of zirconium materials oxidation (see Fig. 1) and accumulation of molecular hydrogen in the contacting environment at radiation-thermal and thermal processes shows that radiation causes to increase of rate of protective oxidation process and accelerates starting of destructive oxidation of zirconium materials in contact with water. In kinetic curves of molecular hydrogen accumulation as a result of heterogeneous processes in contact of metal zirconium and a Zr1%Nb alloy with water vapors, temperature increases to 773 and 1073 K respectively, after certain time recession is observed (see Fig. 1, curve 3). For the purpose of specification of the mechanism of the processes leading to reduction of an yield of molecular hydrogen the thermal desorption is investigated and the analysis of gases, stripped of the processed samples of metal zirconium and a Zr1%Nb alloy is carried out. It is established that in these conditions a certain part of the formed hydrogen collects in the form of hydride in a metal phase and its quantity increases with increase in temperature of process. At T ≥ 1073 K, both at thermal, and in radiation-thermal processes in contact of Zr and Zr1%Nb alloy with water the main part (more than 90%) of the formed molecular hydrogen is in a form of hydride. Time of approach of recession area in kinetic curves decreases with growth of process temperature.

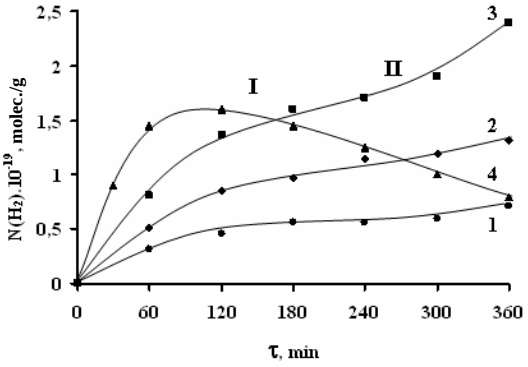

Fig. 2. Kinetic curves of hydrogen accumulation as a result of heterogeneous processes in contact of Zr with water: 1 – thermal process in Zr + H_2O system at T = 473 K; 2 – radiation-thermal process in Zr + H_2O system at T = 473 K; 3 – radiation-thermal process in Zr + H_2O system at T = 773 K; 4 – radiation-thermal process in Zr1%Nb + H_2O system at T = 873 K

On the basis of initial area of kinetic curves a rates of molecular hydrogen accumulation are determined. Dependences of values of initial rate of H_2 accumulation on temperature are given in Fig. 3.

In dependence of rate of H_2 accumulation on temperatures in both systems it is possible to allocate two areas:

1. $T \leq 573\ldots473$ K, where accumulation of H_2 results from radiation-heterogeneous processes, with activation energy E = 7…8 kJ/mol;
2. $T \geq 573$ K, where formation of H_2, results from radiation-thermal and thermal processes.

Activation energy of radiation-thermal processes in the studied interval of temperatures in Zr1%Nb+H_2O system makes E_a = 76 kJ/mol. Nature of temperature dependence of rate and value of activation energy in oxidation processes of metal and accumulation of H_2 at radiation-thermal processes in contact of zirconium materials with water are identical. Activation energies of processes of catastrophic oxidation and the second area of radiation-thermal protective oxidation of zirconium materials are identical and equal to 65 kJ/mol.

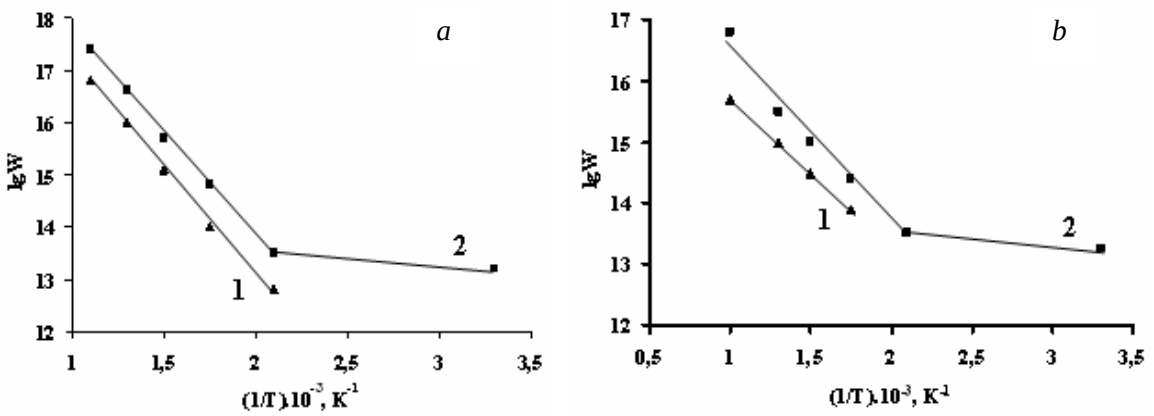

Fig. 3. Temperature dependences of rates of thermal (1) and radiation-thermal (2) processes of hydrogen accumulation in contact of Zr (a) and a Zr1%Nb alloy (b) with water at $\rho_{H_2O} = 5\ mg/cm^3$, $\dot{D}$ *= 7.17 Gy/s*

Considering that in the studied interval of temperatures the rate of pure thermal decomposition is very small [24], observed high values of rates of radiation-thermal and thermal processes of H_2 generation in contact of Zr and Zr1%Nb alloy with water in this interval of temperatures, can be explained by interaction of water molecules with the active centers on a surface of metals formed under the influence of temperature and radiation.

On the basis of the received experimental results of literary materials [11, 21, 24, 25, 27], it is possible to offer the following mechanism of water decomposition in contact with metal materials under the influence of temperature and radiation.

Electrons of conductivity of metals, participating in the thermal movement, are capable to cross a surface and to create a near-surface layer (1…2 Å) of electronic clouds [16, 17]. An action of temperature and radiation can stimulate issue of electrons from metal. Thus the double electric layer – the charged condenser is created. Negative face of the condenser is the electronic cloud, and positive – surface layer of metal ions. Theoretical calculation [16], and also experimental results [20] show that fields in these systems reach $10^8\ldots10^9$ V/cm and have essential impact on superficial processes. Calculation shows [20] that H_2O molecule, in adsorbed state on a surface of metals (Al, Cu), dissociates like $H_2O \rightarrow H^+ + OH^-$ at a field tension $1.3\cdot10^7$ V/cm. Positively loaded Me^+ ions formed on a surface of metals serve as the center of adsorption of a water molecule with formation of the molecular complex Me^+-OH_2. Binding energy between an ion and a molecule of water, extent of transfer of electronic density from a water molecule on Me^+ ion depends from the electron-acceptor properties and radius of an ion [16].

Products of dissociation of water are divided under the influence of electric field on a surface layer of metal. At this condition the H^+ ion, being in direct contact with an electronic cloud of a near-surface layer, can be neutralized:

$$H^+ + e^- \rightarrow H. \quad (2)$$

The superficial positively loaded skeleton interacts both with OH^- ions, and water molecules:

$$Me^+ + OH^- \rightarrow Me–OH; \quad (3)$$

$$2Me – OH \rightarrow Me – O – Me + H_2O; \quad (4)$$

$$Zr^+ + H_2O \rightarrow ZrO^- + H_2. \quad (5)$$

Superficial oxygen holes formed by (5), can migrate in volume as a result of interaction with volume atoms of metals. Influence of density of water vapors and power of γ-irradiation on processes of H_2 accumulation in contact of Zr1%Nb alloy with water is investigated at 873 K.

Dependences of rates of radiation-thermal, thermal and radiation processes of hydrogen accumulation on water density are given in Fig. 4.

Schematically radiation-thermal processes of decomposition of water in contact with metal surfaces, it is possible to present as follows. As a result of radiation-thermal processes on a surface the active centers are formed (S*).

$$Me \overset{T}{\rightleftharpoons} S^*, \quad (6)$$

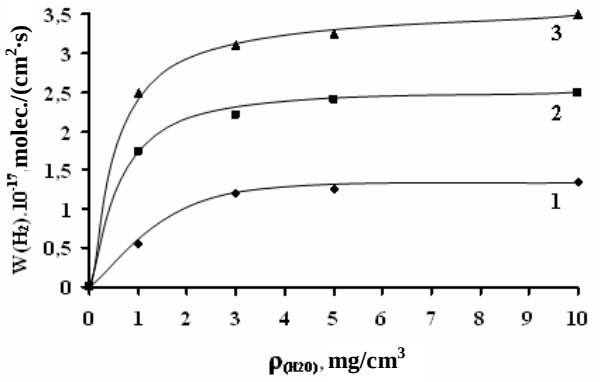

Fig. 4. Dependences of rates of hydrogen accumulation at thermal (1), radiation (2), and radiation-thermal (3) processes of water decomposition in contact with Zr1%Nb alloy from density of water vapors (ρ_{H_2O}) at 873 K, $\dot{D}$ = 7.21 Gy/s

On the formed active centers there is an adsorption of molecules of water with formation of complexes; some of them dissociate further with formation of H_2 (2)–(5):

$$S^* + H_2O_s \rightarrow (S^*\text{-}H_2O), \quad (7)$$

$$2\,(S^*\text{-}H_2O) \rightarrow 2S\text{-}OH + H_2. \quad (8)$$

If to imagine that at the time of adsorption and disintegration of a water molecule on surfaces of metal-oxide systems, comes the stationary mode in the process of generation of the active centers (6), then taking into account (7) and (8) for the rate of processes of H_2 formation, we will receive expression:

$$W_q^s(H_2) = \frac{K \cdot b \cdot \rho_{H_2O}}{1 + b \cdot \rho_{H_2O}}. \quad (9)$$

Here $W_q^s(H_2)$ – rate of H_2 formation (molec./(cm^2·s); b – constant of the adsorptive balance on a surface; ρ_{H_2O} – density of water vapors.

Apparently from experimental curves at $\rho_{H_2O} \le 1$ mg/cm^3 the dependence has linear character $W_i^s(H_2) = K \cdot b \cdot \rho_{H_2O}$ that testifies that $b \cdot \rho_{H_2O} \le 1$ and at $\rho_{H_2O} \ge 3$ we get $b \cdot \rho_{H_2O} \ge 1$ and the rate of process doesn't depend on density of vapors.

Influence of power of radiation is studied at the fixed values of the parameters – T = 873 K, $\rho_{H_2O} = 5$ mg/cm^3. At each value of radiation power the hydrogen accumulation kinetics is studied (Fig. 5,a) and on the basis of initial linear sites of curves a values of rates of processes are defined. In Fig. 5, the dependence $W_i^s = f(\dot{D})$ is presented. Apparently from dependence, in the field of values $\dot{D}$ = 4…10 Gy/s the curve seeks for saturation.

It is possible to explain the observed area of saturation in $W(H_2) = f(\dot{D})$dependence, with approach of balance between processes of generation and recombination death of the active centers on a surface of metals. On the basis of comparison of kinetic curves of H_2 accumulation at radiation-thermal processes at various capacities, it is possible to make the conclusion that balance between processes of generation and death of the active centers on a surface of zirconium materials, is mobile and with increase of $\dot{D}$, the balance (6) comes at small times of contact.

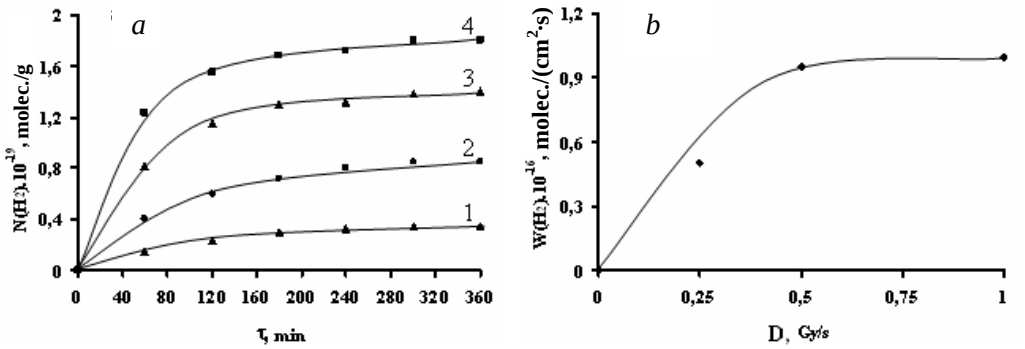

Fig. 5. Influence of power of γ-radiation dose on processes of hydrogen accumulation at radiation-thermal processes of decomposition of water in contact with Zr1%Nb alloy at T = 873 K $\rho_{H_2O} = 5$ mg / cm^3:

a – kinetic curves of hydrogen accumulation in I area: 1 – thermal, 2 – radiation-thermal at $\dot{D}$ = 0.13 Gy/s, 3 – $\dot{D}$ = 2.19 Gy/s, 4 – $\dot{D}$ = 3.47 Gy/s, 5 – $\dot{D}$ = 7.17 Gy/s; b – dependence $W(H_2) = f(\dot{D})$

Influence of radiation power and temperature on processes of H_2 accumulation as a result of destructive oxidation of the studied materials is investigated. It is established that in zirconium metal, the area of destructive oxidation under identical conditions comes at smaller values of time of contact, than in Zr1%Nb alloy that testifies to passivity of an alloy to radiation-thermal processes of corrosion in comparison with pure zirconium. Time of approach of destructive oxidation area as a result of radiation-thermal processes in contact of these materials with water decreases with increase of temperature; the transitional area completely disappears

at $T \geq 723$ K in Zr + H_2O-system, and at $T \geq 1073$ K in Zr1%Nb + H_2O-system.

On the basis of the received regularities of radiation-thermal processes of H_2 accumulation in contact of metal materials with water, it is possible to define concentration of molecular hydrogen in the coolant in actual practice of work of nuclear reactors. On the basis of values of radiation component rates in radiation-thermal processes (9), conditional value of a yield of molecular hydrogen per the energy absorbed by water in Zr + H_2O-system is calculated. Taking into account that the power of a dose of β- and γ-radiation in aqueous reactors, usually makes 125 W/kg [27–29], the rate of H_2 formation in 1 kg of the coolant is calculated as a result of radiation-thermal processes in contact with Zr metal (Tabl. 1).

Table 1

Quantity of the formed H_2 in 1 kg of the coolant as a result of radiation chemical processes in contact of zirconium with water

T, K	ρ_{H_2O}, mg/cm^3	$\dot{D}$, W/kg	$W(H_2)$, g·kg^{-1}·h^{-1}
300	$1 \cdot 10^3$	125	0.05
473	5		0.05
573	5		0.39
773	5		39.21
923	5		54.13

As shown from the table, molecular hydrogen in amount of $m_{H2} \approx 0.40$ g/hour is formed at temperature conditions of work of nuclear reactors ($T \leq 573$ K) in 1 kg of the coolant as a result of radiation and thermal processes in contact of zirconium with water. In accident mode the amount of hydrogen formed as a result of radiation and thermal processes in contact of zirconium with water in 1 kg of the coolant, exceeds $m_{H_2} \approx 40$ g/hour.

Values of rates of thermal processes of oxidation, in comparison with the rate of radiation-thermal processes become insignificant for Zr at $T \geq 473$ K and for Zr1%Nb alloy at $T \geq 573$ K, and they within the accuracy of definition can be neglected.

The effect of radiation in the first area of oxidation of Zr and Zr1%Nb alloy in contact with water decreases with growth of temperature and becomes imperceptible at $T \geq 873$ and $T \geq 1073$ K respectively.

The effect of radiation in radiation-thermal processes depends on the power of radiation [29–31]. For the purpose of detection of regularities of power of radiation influence on radiation-thermal processes of oxidation of an Zr1%Nb alloy in the first area, the kinetics of corrosion of an Zr1%Nb alloy is investigated at T = 873 K and various capacities of γ-radiation power $\dot{D}$ = 0.14…7.16 W/kg.

In Tabl. 2 values of rate of zirconium oxidation in initial area of kinetic curves and values of effect of radiation at corrosion of the Zr1%Nb alloy [22, 23, 26, 28] are given.

Apparently from the table the effect of radiation in the process of corrosion of the Zr1%Nb alloy in contact with water is observed only in a certain area of values of power of radiation and reaches 100% at the power of γ-radiation $\dot{D} \geq 3.48$ W/kg:

$$R = \frac{W_R - W_T}{W_T} \cdot 100\%, ,$$

where W_R – the rate of radiation-thermal; W_T – the rate of thermal processes of oxidation of the Zr1%Nb alloys.

Table 2

Influence of power of γ-radiation on process of radiation-thermal corrosion of Zr1%Nb alloy in contact with water at T = 873 K, $\rho_{H_2O} = 5$ mg/cm^3

Power of radiation, W/kg	$W_{corr} \cdot 10^4$, mg·cm^{-2}·s^{-1}	R	Power of radiation, W/kg	$W_{corr} \cdot 10^4$, mg·cm^{-2}·s^{-1}	R
0	5	0	3.48	10	100
0.14	5.9	0	7.16	10	100
2.19	7.3	46	–	–	–

CONCLUSIONS

Apparently from the given results, radiation and radiation-thermal processes in contact of zirconium materials with water lead to acceleration of process of molecular hydrogen formation and oxidation of metal, as in the field of protective oxide layer formation on a surface, and in the field of destructive oxidation of these materials in contact with water vapors which happens at T > 873 K. Action of radiation causes also acceleration of approach of destructive oxidation of zirconium materials in contact with water.

The found effect of radiation in the process of hydrogen accumulation and oxidation of metals in contact of zirconium materials with water vapors at various temperatures can be used in the field of radiation materials science and at specification of the scenario of accidents in nuclear reactors.

Considering that in both cases an interaction of the coolant with materials of the heat allocating elements happens in the conditions of splitting of nuclear

materials, the contribution of radiation processes as a result of a fragmental radiolysis of water will be more, than in processes of γ-radiolysis. Thus, in actual practice of accidents the rate of destruction of constructional materials and accumulation of hydrogen will be more, than in the model experiments observed by us.

REFERENCES

1. V.V. Gerasimov. *Corrosion of reactor materials*. M.: "Atomizdat", 1980.
2. Z. Alexan. Radiolysis and corrosion processes in reactors" // *STU Cer. "Fiz"*. 1970, v. 22(9), p. 1005.
3. B. Cox. Factors controlling the corrosion behavior of zirconium alloys under irradiation // *Proceedings of Materials Science Conf.*, Alushta, 1978, v. 5, p. 91-131.
4. H.C. Christensen. Effects of water radiolysis on corrosion in nuclear reactors // *Radiat. Phys. Chem.* 1981, v. 18(1-2), p. 147-158.
5. A.F. Nechaev, N.G. Petrik, V.M. Sedov, T.B. Sergeeva. *Radiation corrosion of structural materials for nuclear power plants*. M.: "TSNII atominform", 1988, 54 p.
6. S.A. Kabakchi, M.A. Budayev, O.M. Kovalevich. The formation of hydrogen in thermoradiation processes at hypothetical accidents with loss of coolant at nuclear power plants with WCR reactors // *High Energy Chemistry*. 1988, v. 22, N 4, p. 295-300.
7. V.M. Sedov, A.F. Nechaev, N.G. Petrik, T.B. Sergeeva. *Radiation Chemistry of coolants of nuclear power plants*. L.: "LTI im. Lensoveta", 1986, 62 p.
8. A.A. Kulskiy, E.V. Strahov, A.M. Voloshinova, V.A. Bliznukova. *Water in nuclear power*. Kiev: "Naukova Dumka", 1983, p. 43.
9. B.A. Alekseev, E.I. Viegin, V.A. Ermakov. Water regimes and corrosion of metals in WCR // *Water regime of WCR, radiation control of coolants. Sympos. SEV, GDR*, 8–9 may 1972, p. 9-53.
10. Ph. Cassette. *Etude de la production du comportment de J'hydrogen dans un reacteur nucleativ a can pressurisee on situation accidentell*: Rapport CEA-R-S175, CEN-Saclay, 1982.
11. W.Q. Berns, P.B. Moore. Water radiolysis and its effects upon in reactor zircaloy corrosion // *Radiation Effects*. 1976, v. 30, p. 233-242.
12. I. Ishigure, N. Eujita, T.A. Tamura, et al. Effects of gamma-radiation on the release of corrosion products from carbon steel and stainless steel in high temperature // *Nucl. Technol*. 1980, v. 50, p. 169-177.
13. A.K. Pikaev. *Dosimetry in radiation chemistry*. M.: "Nauka", 1975, 120 p.
14. S. Leistikov, G. Schanz. The oxidation behavior of zircaloy-4 in steam between 600 and 1600 ^{0}C // *Workstoffe and Korrosion.* 1985, v. 36, N 3, p. 105-116.
15. C. England. Thermodynamics of water decomposition catalyzed by zeolites // *Int. J. Hydrogen Energy*. 1984, v. 9, N 4, p. 315-317.
16. V.P. Kovalev. *Secondary electrons*. M.: "Energoizdat", 1987, 282 p.
17. N. Ashkroft, N. Mermin. *Solid State Physics*. M.: "Mir", 1979, 339 p.
18. Y. Maeno, M. Yamamoto, S.M. Naito, M. Mabuchi, T. Hashino. Change in the work function of zirconium by oxidation at high temperatures and low oxygen pressures // *J. Chem. Soc. Faraday Trans*. 1991, v. 87, N 9, p. 1399-1403.
19. V.F. Urbanic, J.E. Le Surf, A.B. Johnson. Effect of aging and irradiation on the corrosion of Zr-2.5wt.%Nb // *Corrosion (USA).* 1975, v. 31, N 1, p. 15-20.
20. V.M. Pinchuk, Y.A. Kruglak, M.D. Dolgushin. Spatial and electronic structure of ion complexes Li^+, Na^+, Be^{2+} и Mg^{2+} with molecules of HF, H_2O and NH_3 // *Theoretical and Experimental Chemistry*. 1976, v. 12, issue 2, p. 155-162.
21. V.F. Sedov, A.F. Nechaev, N.T. Petrik, T.R. Sergeeva. *Radiation Chemistry of Coolants of Nuclear power plants.* L.: "LTI im. Lensoveta", 1987, p. 58.
22. V.F. Zelinskiy, I.A. Petelguzov, L.P. Rekova, A.G. Rodele. The effect of ion implantation on corrosion of zirconium and its alloys *// Problems of Atomic Science and Technology. Series "Physics of Radiation Effect and Radiation Materials Science".* 1989, issue 1 (48), p. 47-52.
23. R. Adamson, G. Friedrich, C. Brian // *Corrosion Mechanisms in Zirconium Alloys*. 2007, p. 1-19.
24. J.A. Laverne. H_2 formation from the radiolysis of liquid water with zirconium // *J. Phys. Chem. B.* 2005, v. 106, p. 380-386.
25. B.A. Cox. Mechanisms for the hydrogen uptake process in zirconium alloys // *J. Nucl. Mater*. 1999, v. 264, p. 283-294.
26. B.A. Cox. Mechanisms of Zirconium Alloy Corrosion in Nuclear Reactors // *Journal of Corrossion Science and Engineering*. 2003, v. 6, p. 14-21.
27. B. Cox. Some thoughts on the mechanism of in-reactor corrosion of zirconium alloys // *J. Nucl. Materials.* 2005, issue 336, p. 331-368.
28. R.B. Adamson, B. Cox, F. Garzarolli, A. Strasser, P. Rudling. *Corrosion Mechanisms in Zirconium Alloys, IZNA$_7$*: Special Topic Report, 2002, 45 p.
29. M. Blat and D. Noel. Detrimental role of hydrogen on the corrosion rate of Zr alloys // *ASTM STP 1295.* 1996, p. 319-337.
30. M. Blat, L. Legras, D. Noel, H. Amanrich. Contribution to a Better Understanding of the Detrimental Role of Hydrogen on the corrosion Rate of Zircaloy-4 Cladding Materials // *12th Int. Symposium on Zirconium in the Nuclear Industry, ASTM STP 1354*. Toronto, Canada, 1998, p. 563.
31. P. Bossis et al. Study of the Mechanism controlling the oxide growth under irradiation // *ASTM STP 1423*. 2002, p. 190-221.

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ЗАКОНОМЕРНОСТИ РАДИАЦИОННО-ГЕТЕРОГЕННЫХ ПРОЦЕССОВ В КОНТАКТЕ Zr И СПЛАВА Zr1%Nb С ВОДОЙ

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Исследовано влияние радиации в процессе накопления водорода и окисления циркония в результате гетерогенных процессов в контакте циркония и сплава Zr1%Nb с водой. Выявлен вклад радиационных процессов в этих контактах на радиолизные и терморадиолизные процессы разложения воды. Установлено, что радиационные процессы в контакте циркониевых материалов с водой вызывают ускорение процессов накопления H_2 как в результате образования защитной оксидной пленки на поверхности, так и разрушительного окисления.

ЗАКОНОМІРНОСТІ РАДІАЦІЙНО-ГЕТЕРОГЕННИХ ПРОЦЕСІВ У КОНТАКТІ Zr І СПЛАВУ Zr1%Nb З ВОДОЮ

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Досліджено вплив радіації в процесі накопичення водню і окислення цирконію в результаті гетерогенних процесів у контакті цирконію і сплаву Zr1%Nb з водою. Виявлено внесок радіаційних процесів у цих контактах на радіолізні та терморадіолізні процеси розкладання води. Встановлено, що радіаційні процеси в контакті цирконієвих матеріалів з водою викликають прискорення процесів накопичення H_2 як внаслідок утворення захисної оксидної плівки на поверхні, так і руйнівного окислення.