Radiation-heterogenic processes of hydrogen accumulation in water-cooled nuclear reactors

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Abstract. The research into the influence of radiation on the process of hydrogen accumulation and zirconium oxidation as a result of heterogeneous processes taking place in contact of zirconium and Zr + 1%Nb alloy with water vapour was conducted. Due to such contact the contribution of radiation processes into radiolysis and thermo-radiolysis of water decomposition processes was revealed. It was determined that radiation-heterogenic processes in contact of zirconium materials with water invoked earlier accumulation of hydrogen originating from both the protective oxidation film on surface formation and destructive oxidation of metallic materials.

Key words: zirconium • corrosion • water-cooled nuclear reactor • hydrogen • radiolysis

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Introduction

The study of physico-chemical processes occurring during contact of metal constructional materials of nuclear reactors with water influenced simultaneously by temperature and radiation is of big significance for solving material science problems and safety of power reactor facilities. It is a peculiarity of such processes that they can lead either to corrosion of constructional materials, or accumulation of explosive gas products in the medium [1–13, 15–19, 22, 24–27, 29–31, 33, 36, 37, 40, 41, 44, 45].

Determining molecular hydrogen accumulation regularity with the coolant being influenced by radiation and temperature and in contact with metal constructional materials, both at normal and emergency operating conditions of a nuclear power reactor, is of high importance both in terms of identifying safe operational modes and assessing accidents with core damage.

Review of relevant literature [1, 3–5, 7–12, 15–18, 25–27, 29, 33, 36, 40, 41, 44, 45] shows that the radiolysis processes in water, both in a liquid and vapour state, as well as vapour-metal reactions, are considered to be the source of molecular hydrogen in water-cooled nuclear reactors. In the papers radiolytic processes of hydrogen accumulation in a nuclear reactor are characterized by hydrogen yield, observed in homogeneous water radiolysis [27]. Still, the influence of radiation and radiation-thermal processes at contacts of constructional materials with water, on hydrogen accumulation processes, was not taken into account.

Neither the mechanisms for radiation influence and collective radiation-temperature action on vapour-metal reactions are known.

In our paper the mechanisms for radiation (R), radiation-thermal (RT) and thermal (T) processes of molecular hydrogen accumulation in contact of reactor zirconium and Zr + 1%Nb alloy with water are studied.

Experimental methods

The research was conducted under static conditions in the specific quartz ampoules of the volume of $0.25 \div 0.30$ cm^3. Reactor zirconium of 99% purity and zirconium alloy containing 1% of thin tape Nb were examined. The contact surface of the samples was identified by their geometrical size. In order to exclude organic surface contaminants contribution to the process of hydrogen accumulation, the samples were preliminarily cleaned with organic solvents, such as ethanol and acetone, and then washed down with distilled water. The samples were dried at the temperature of $300 \div 320$ K in the argon medium. The dried samples were weighted with the accuracy of $\pm 5 \times 10^{-3}$ g and then closed in quartz ampoules. The quartz ampoules were degassed up to $P \approx 10^{-3}$ Pa, subsequently at $T = 300$ K and $T = 673$ K. Radiation and radiation-thermal processes were carried out by using γ-irradiation source of ^{60}Co. The dosimetry of the source was performed with chemical dosimeters such as ferrosulphate, cyclohexane and methane. The dose for the studied system was recalculated by comparing electron densities with dosimetric systems [37]. Simultaneously, the irradiation dose was determined by theoretical calculation [14]. The difference between the calculated and experimental values of the absorbed irradiation dose did not exceed 10%, which evidenced the permissible coincidence of values.

Gas products of the processes were transferred into the special graduated volumes and analysed with gas chromatography (Gazochrom 3101). During radiolytic processes at $T = 300$ K the gas composition products included hydrogen and oxygen, however during thermo-radiolysis the gas products contained mostly hydrogen.

Results and discussions

The kinetics of hydrogen accumulation during graduated decomposition of water in the presence or absence of in-reactor zirconium at the temperature of 300 K was investigated in order to find the influence of metal materials on water radiolysis. Reaction rates and radiation-chemical yields of hydrogen, calculated on the basis of kinetic curves (Fig. 1), were equal to 0.55 and 0.44 molecule/100 eV, respectively. The increase in the radiation-chemical yield for hydrogen from water radiolysis in metal materials presence in comparison to hydrogen yield for "pure" water radiolysis can be explained by the contribution of δ-electrons emitted from metal induced by γ-quanta and other water decomposition centres formed on the metal surface. The increase in the water radiolysis rate on the surface of
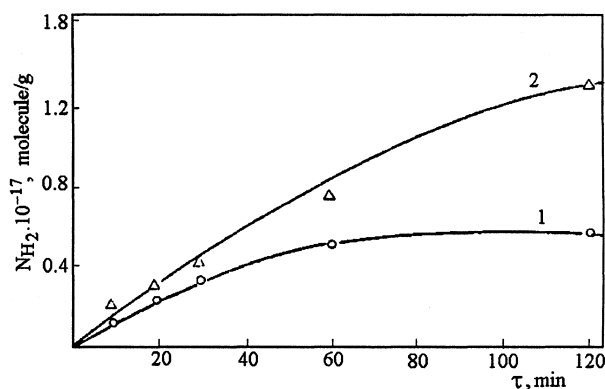
Fig. 1. Kinetics of hydrogen accumulation in radiolysis of pure water (1) and Zr-H$_2$O system (2) at $T = 300$ K, $\dot{D} = 8.88$ Gy/s, $m_{H_2O} = 0.1$ g, $m_{Zr} = 0.06$ g.

metal zirconium and Zr + 1%Nb alloy are equal to $\Delta W = 3.44 \times 10^{12}$ molecule/cm^2 and 5.00×10^{12} molecule/cm^2, respectively.

Metal elements of construction in contact with coolant during the standard operation of nuclear reactors are simultaneously exposed to temperature and radiation. Therefore, to determine the mechanism for radiation-thermal surface processes of hydrogen formation at water-metal materials contact is of particular concern.

For this purpose we studied the kinetics of molecular hydrogen accumulation at radiation-thermal and thermal processes at zirconium and Zr + 1%Nb alloy contacts with water and from the initial linear sections of the experimental kinetic curves we determined $W_{RT}(H_2)$ and $W_T(H_2)$ values, which are the rates of the respective processes.

The rate of the radiation component $W_R(H_2)$ in the radiation-thermal process of hydrogen accumulation can be conditionally established as the difference between the rates of the radiation-thermal and thermal processes.

$$(1) \qquad W_R(H_2) = W_{RT}(H_2) - W_T(H_2)$$

The kinetics of oxide formation on the surface of the studied materials resulting from the radiation-thermal and thermal processes due to surface-water contact were investigated with the gravimetric method (Fig. 2). The experimental results show that oxide film formation and hydrogen accumulation due to concerned processes is stoichiometric and determined by the equation:

$$(2) \qquad Zr + 2H_2O \xrightarrow{T} ZrO_2 + 2H_2$$
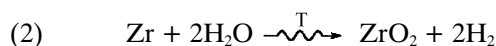
It has been found that the thermal processes contribution to molecular hydrogen accumulation and metal oxidation process in the water – clean surface contact, for metal zirconium and Zr + 1%Nb alloy, is measurable from $T = 473$ K and increases with rising temperature. At temperature $T \geq 1073$ K the radiation component of the radiation-thermal process in comparison with the thermal component becomes insignificant $W_T(H_2) >> W_R(H_2)$. In the kinetic curves of molecular hydrogen accumulation and zirconium materials oxidation at radiation-thermal processes (Fig. 2) two areas can be conventionally distinguished [29], namely, I – the area corresponding to hydrogen accumulated in
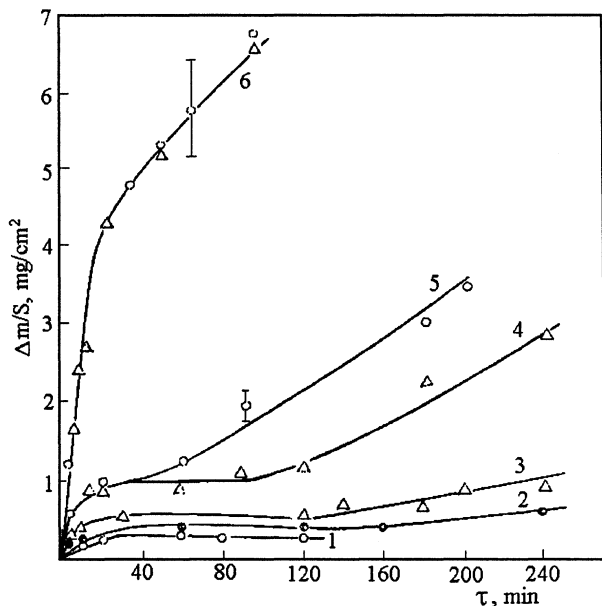
Fig. 2. Kinetics curves of Zr + 1%Nb alloy oxidation for radiation-thermal ($\dot{D}$ = 7.16 Gy/s): $1 - T = 473$ K; $3 - T = 873$ K; $5 - T = 1073$ K; $6 - T = 1273$ K and thermal processes; $2 - T = 873$ K; $4 - T = 1073$ K in contact with water ($\rho_{H_2O} = 5$ mg/cm^3).

heterogeneous processes with formation of a protective oxidation phase on the surface of zirconium materials; and II – the area of hydrogen accumulated in destructive oxidation of materials.

The first area of zirconium materials oxidation in contact with water resulted in formation of black oxidation film with oxygen deficit ($ZrO_{1.95}$) [12]. This film protects zirconium from further oxidation. The completion of the protective oxidation film on the zirconium surface corresponds to the saturation region of the kinetic curves. Due to adverse conditions, pores massively accumulate in the oxidation film and $Zr-ZrO_2$ system being not only in prolonged contact with water but also influenced by radiation and temperature, a destructive oxidation starts in zirconium materials. The comparison of the kinetic curves of zirconium materials oxidation (Fig. 3) and molecular hydrogen accumulation in the contacting medium at radiation-thermal and thermal processes shows that radiation induces an increase in the rate of protective oxidation process and accelerates the effect of destructive oxidation of zirconium
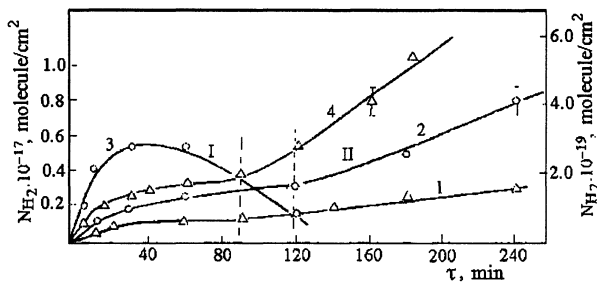

Fig. 3. Kinetic curves of hydrogen accumulation resulting from heterogeneous processes in contact of zirconium and Zr + 1%Nb alloy with water. 1 – thermal process in the system of Zr–H$_2$O at $T = 473$ K; 2 – radiation-thermal process in the system of Zr–H$_2$O at $T = 473$ K; 3 – radiation-thermal process in the system of Zr–H$_2$O at $T = 773$ K; 4 – radiation-thermal process in the system of Zr + 1%Nb–H$_2$O alloy at $T = 873$ K.

materials contacting water. The dip in the kinetic curves of the molecular hydrogen accumulation is observed (Fig. 3, curve 3) as a result of heterogeneous processes occurring at metal zirconium and Zr + 1%Nb alloy contacts with water vapour for temperatures above 773 and 1073 K, respectively. It takes place after a definite contact time. Still, a decrease in the molecular hydrogen yield for these ranges of contact time and temperature values was not accompanied by weight reduction. To properly define the mechanisms for processes causing decreased molecular hydrogen yields, thermal desorption and the analysis of gases desorbed from the pretreated samples of zirconium and Zr + 1%Nb alloy were investigated. It was determined that under such conditions a certain part of hydrogen is accumulated as a hydride in the metallic phase and the amount increases with rising temperature. At $T \geq 1073$ K for both thermal and radiation-thermal processes at water contacts with zirconium and Zr + 1%Nb alloy, a major part (over 90%) of the formed molecular hydrogen is in the hydride form. The time point of the dip in the kinetic curves decreases as the temperature of the processes rise.

The molecular hydrogen accumulation rate in the radiation-thermal and thermal processes was determined from the initial region of the kinetic curves. The dependence of the initial hydrogen accumulation rate on temperature is shown in Fig. 4.

In both systems two regions of the temperature dependence curve for hydrogen accumulation rate can be recognised. Namely, the area I within the temperature $T \leq 573$–473 K, where hydrogen accumulation occurs to be the result of the radiation-thermal processes with activation energy $E = 7$–8 kJ/mol, and the area II of $T \geq 573$ K where hydrogen formation results from
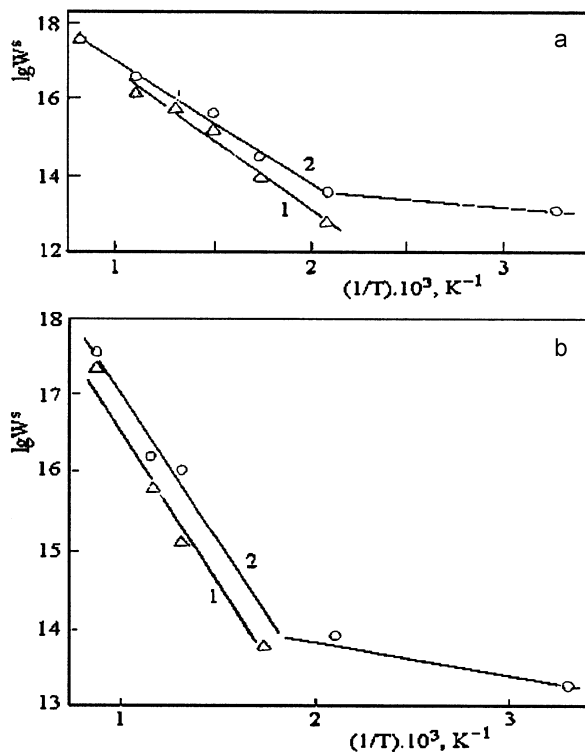
Fig. 4. Temperature dependence of thermal (1) and radiation--thermal (2) processes for hydrogen accumulation in contact of zirconium (a) and alloy (2) with water at $\rho_{H_2O} = 5$ mg/cm^3, $\dot{D} = 7.17$ Gy/s.

radiation-thermal and thermal processes. The activation energy in Zr + 1%Nb + H₂O systems both for radiation--thermal processes (second temperature range) and for thermal processes remains the same and is equal to $E_a \approx$ 68 kJ/mol. The activation energy of the radiation-thermal processes in Zr + H₂O system is lower and amounts to $E_a = 58$ kJ/mol. The temperature dependence rate and the activation energy values for metal oxidation processes for radiation-thermal processes in contact of zirconium materials with water and for hydrogen accumulation are identical in character. Activation energies of the destructive oxidation processes and the second area of the radiation-thermal protective oxidation of zirconium materials are the same and equal to 65 kJ/mol.

Considering that the rate of pure water thermal decay in the investigated temperature range is really small [27], the high values of radiation-thermal and thermal processes of hydrogen generation in contact of zirconium and Zr + 1%Nb alloy with water in the respective temperature range, could be explained by water molecules interacting with the metal surface active states induced by temperature and radiation.

The influence of water vapour density and γ-radiation power on the hydrogen accumulation processes in contact of Zr + 1%Nb alloy with water at 873 K was also investigated.

The dependence of radiation-thermal, thermal and radiation processes of hydrogen accumulation rate on the water density are given in Fig. 5.
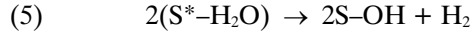
Radiation-thermal processes of water decomposition due to contact with metal surface can be schematically shown as follows: active centres (S*) induced by radiation and thermal processes are formed on the surface

$$(3) \qquad \mathrm{Me} \xrightarrow{\ \ T\ \ } \mathrm{S^*}$$

Adsorption of water molecules with formation of (S*–H₂O) complexes occurred on the formed active centres. Some of (S*–H₂O) complexes are dissociated with the hydrogen formation.
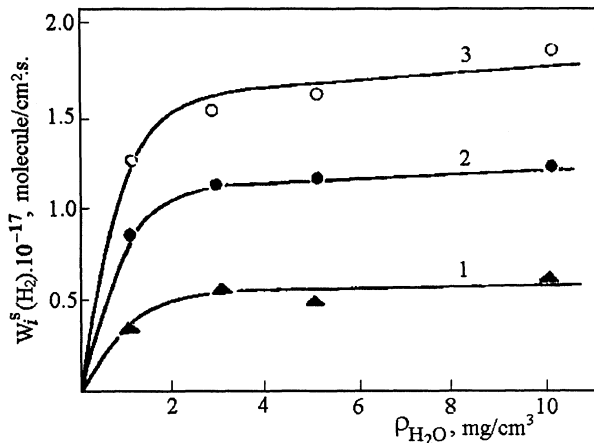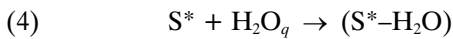
$$(4) \qquad \mathrm{S^*} + \mathrm{H_2O}_q \rightarrow (\mathrm{S^*{-}H_2O})$$

$$(5) \qquad 2(\mathrm{S^*{-}H_2O}) \rightarrow 2\mathrm{S{-}OH} + \mathrm{H_2}$$

When assumed that the stationary mode for the process of generating active centres (3) coincides with the moment of adsorption and molecule decay on the surface of oxide systems then, taking into account (4) and (5), the following expression is obtained for the rate of hydrogen formation processes:

$$(6) \qquad W_i^s(\mathrm{H_2}) = \frac{K \times b \times \rho_{\mathrm{H_2O}}}{1 + b \times \rho_{\mathrm{H_2O}}}$$

where: $W_i^s(\mathrm{H_2})$ is the hydrogen formation rate (molecule·cm⁻²·s⁻¹); b – is the constant of adsorption equilibrium on the surface; $\rho_{\mathrm{H_2O}}$ – is the density of water vapour.

From the experimental curves at ≤ 1 mg/cm³ it can be observed that the dependence is linear in character $W_i^s(\mathrm{H_2O}) = K \times b \times \rho_{\mathrm{H_2O}}$, which proves that $b \times \rho_{\mathrm{H_2O}} \leq 1$, and at $\rho_{\mathrm{H_2O}} \geq 3$, $b \times \rho_{\mathrm{H_2O}} \geq 1$ the process rate does not depend on the density of water vapour $W_i^s(\mathrm{H_2}) =$ const.

The influence of radiation power was investigated at the fixed values of the parameters, i.e. $T = 873$ K, and $\rho_{\mathrm{H_2O}} = 5$ mg/cm³. The kinetics of hydrogen accumulation (Fig. 6a) was studied at each value of the radiation power. The processes rate values were determined from the initial parts of the curves. The dependence of $W(\mathrm{H_2}) = f(\dot{D})$ is shown at the Fig. 6b. As shown the dependence curve tends to saturate in the range of values $\dot{D} = 4 \div 10$ Gy/s.

The observed saturation area for the dependence curve of $W(\mathrm{H_2}) = f(\dot{D})$ can be explained by equilibrium established between the processes of generating
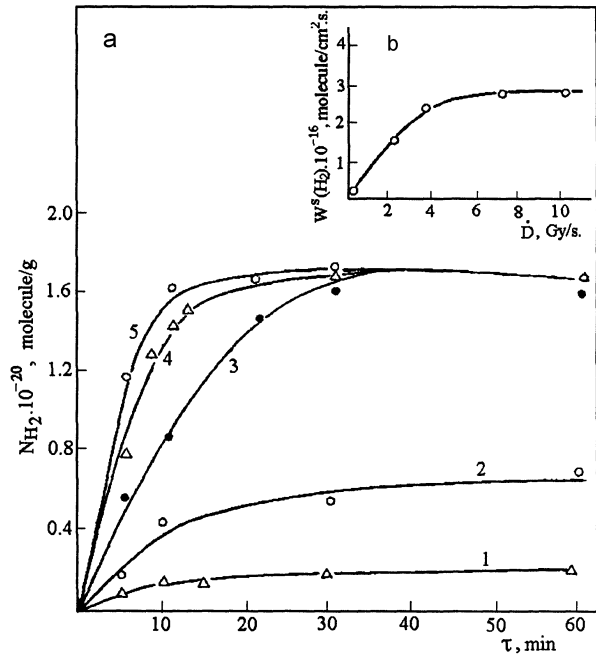
Fig. 6. The influence of γ-radiation dose rate on the hydrogen accumulation processes in radiation-thermal processes of water decomposition in contact with Zr + 1%Nb alloy at $T = 873$ K, $\rho_{\mathrm{H_2O}} = 5$ mg/cm³. (a) Kinetic curves for hydrogen accumulation in area I: 1 – thermal; 2 – radiation-thermal 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) The dependence of $W(\mathrm{H_2}) = f(\dot{D})$.

Fig. 5. The dependence of hydrogen accumulation rates for thermal (1), radiation (2) and radiation-thermal (3) processes of water decomposition in contact with Zr + 1%Nb alloy on density of water vapour $\rho_{\mathrm{H_2O}}$ at 873 K, $\dot{D} = 7.21$ Gy/s.

Table 1. Quantity of hydrogen (for 1 kg of coolant) formed as result of radiation-chemicals processes in contact of Zr with water

T (K)	ρ_{H_2O} (mg/cm³)	$\dot{D}$ (W·kg⁻¹)	W (H₂) (g·kg⁻¹·h⁻¹)
300	1×10^3		0.05
473	5		0.05
573	5	125	0.39
773	5		39.21
923	5		54.13

and recombination loss of active centres on the metal surface. By comparing the kinetics curves for hydrogen accumulation in radiation-thermal processes for different radiation power, it can be concluded that the equilibrium between the processes of generating active centres and their recombination loss on the surface of zirconium materials has been active and attained (6) at low contact time with increasing $\dot{D}$.

The radiation power and temperature effects upon the hydrogen accumulation processes resulting from destructive oxidation in the researched samples has also been studied. It has been determined that the destructive oxidation area in metal zirconium under identical conditions starts at smaller values of contact time than in Zr + 1%Nb alloy, which proves that the alloy is more passive to radiation-thermal processes of corrosion than pure zirconium. The time of establishment of area of destructive oxidation as a result of radiation-thermal processes of these materials with water decreased with the temperature increasing in the system of Zr–H₂O at $T \geq 723$ K, and the transition area disappeared completely in the system of Zr + 1%Nb–H₂O at $T \geq 1073$ K.

Such a regularity of radiation-thermal processes for molecular hydrogen accumulation in contact of metallic materials with water, allows to determine concentration of molecular hydrogen in coolants at real operation conditions. Having defined the rate values for radiation components in radiation-thermal processes (1) conventional value of molecular hydrogen yield on the energy absorbed by water in Zr–H₂O system were calculated. With a typical dose rate of β- and γ-radiation in water cooled reactors set to 125 W·kg⁻¹ [1–5, 8, 10–13, 16, 17, 22, 25–27, 32, 36], we calculated the rate of hydrogen formation due to radiation-thermal processes in contact with metal zirconium, per 1 kg of coolant (Table 1).

For Zr at $T \leq 473$ K and Zr + 1%Nb at $T \leq 573$ K the rate of thermal oxidation processes in comparison with the rate of radiation-thermal processes is insignificant, thus these processes can be neglected, at least within the given precision range.

The radiation effect in the first area of oxidation for Zr and Zr + 1%Nb alloy, both systems in contact with water, decreases with the increased temperature to fall below the measurable value at $T \geq 873$ K and $T \geq 1073$ K, respectively.

The radiation effect in radiation-thermal processes depends on the radiation power [14, 42]. To identify the presumed regularities in radiation power influence on radiation-thermal processes for Zr + 1%Nb alloy oxidation in the first area, the kinetics of Zr + 1%Nb alloy corrosion at $T = 873$ K and different γ-radiation powers $\dot{D} = 0.14$–7.16 W·kg⁻¹ were examined.

The rates of zirconium oxidation in the initial area of the kinetic curves and values of radiation effect within

Table 2. The influence of γ-radiation power on the process of radiation-thermal corrosion for Zr + 1%Nb alloy in contact with water at temperature $T = 873$ K, $\rho_{H_2O} = 5$ mg/cm³

Radiation power (W·kg⁻¹)	$W_{corr.} \times 10^4$ (g·cm⁻²·s⁻¹)	R
0	5.0	0
0.14	5.9	0
2.19	7.3	46
3.48	10.0	100
7.16	10.0	100

the corrosion of Zr + 1%Nb alloy are presented in Table 2 [46].

$$(7) \qquad R = \frac{W_{RT} - W_T}{W_T} \cdot 100\%$$

where: W_{RT} – radiation-thermal rate; W_T – thermal processes rate for Zr + 1%Nb alloy oxidation.

As shown in the table, the radiation effect for Zr + 1%Nb alloy corrosion process due to contact with water, is observed only within a defined range of power values of radiation and reaches 100% at γ-radiation power $\dot{D} \geq 3.48$ W·kg⁻¹.

Due to radiation influence the area of destructive oxidation for zirconium and Zr + 1%Nb alloy occurs much earlier. The shift in the initiation of destructive oxidation (DO) under the influence of radiation depends on temperature. Influence of γ-radiation at the temperatures $T \leq 723$ K initiates a displacement of DO beginning in the area of low time of contact $\tau_{(DO)}$ ($\tau_{(DO)}$ decreases ~ 2–3 times). The beginning of destructive oxidation and the difference in $\tau_{(DO)}$ values for radiation-thermal and thermal processes decreases with rising temperature. At $T \geq 1273$ K no transition zone to DO is observed (Fig. 2) and the radiation effect for the processes in zirconium materials contacting with water is imperceptible.

In the literature [33] the destructive oxidation of zirconium-4 within thermal processes in contact with water steam was reported. Figure 7 shows the reported results [33] plotted against our findings for comparison. The kinetic curves of alloy oxidation in algorithmic coordinates at $T = 873$ K for zirconium-4 alloys and Zr + 1%Nb, within the accuracy range; coincide. The observed insignificant deflection in the values of metal quantity undergoing oxidation at high temperature can be explained by the difference in alloys composition.

Both our experimental results and the results reported elsewhere [1, 7, 9, 15, 18, 19, 24, 29, 37, 40, 44, 45] make us suggest the following mechanism for water decomposition in contact with metal materials influenced by radiation and temperature.

Metal conductance electrons participating in the thermal motion are capable of crossing the surface
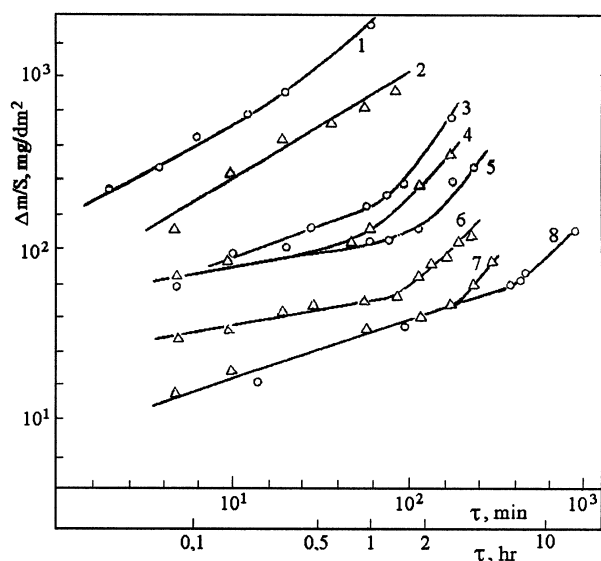
Fig. 7. Isothermal kinetic curves of thermal and radiation-
-thermal processes for zirconium alloy oxidation in contact
with water steam plotted in logarithmic coordinates: 1 – zir-
conium-4, thermal T = 1273 K (lit.); 2 – Zr + 1%Nb alloy,
radiation-thermal and thermal T = 1273 K; 3 – zirconium-4,
thermal T = 1073 K (lit.); 4 – Zr+1%Nb alloy, radiation-
-thermal T = 1073 K; 5 – Zr + 1%Nb alloy, thermal T =
1073 K; 6 – Zr + 1%Nb alloy, radiation-thermal T = 873 K; 7 –
zirconium-4 (lit.); 8 – Zr + 1%Nb alloy, thermal T = 873 K.

and forming a near-surface electron cloud layer (1–2 Å)
[6, 30, 31, 35]. Electron emission from metal can be
stimulated by radiation and temperature. Thus, a double
electric layer – a charged capacitor is formed. The
electron cloud serves as a negative capacitor plate and
surface layer of metal ions as a positive one. Theoretical
calculations [38], along with the experimental results
[39] shows that the field in such systems can reach up
to 10^8–10^9 V/cm, which exerts the essential influence
on surface processes. The calculation [32] shows that
H_2O molecule adsorbed on the metal surface (Al, Cu)
dissociates water $H_2O \rightarrow H^+ + OH^-$ at the voltage
1.3×10^7 V/cm of the field. The positive ions Me^+,
formed on the surface of metals, serve as an adsorp-
tion centre of electro-donor water molecules with the
formation of molecular complex $Me^+ \cdots OH_2$. Energy
of the ions and water molecules bond, and the degree of
electron density transfer from the water molecule onto
the Me^+ ion, depend on electron acceptor properties
and ionic radius [38].

The products of water dissociation are separated
under the influence of electric field on the surface layer
of metal. Under such conditions H^+, being in direct
contact with electron cloud of near-surface layer, can
be neutralized:

(8) $H^+ + e^- \rightarrow H$

Usually, charged positive atoms on the surface of
metallic materials can be formed under the ionizing ir-
radiation and temperature. The positive charged surface
state was observed experimentally and theoretically
researched. Under the influence of gamma quantum
surface positive states can be excited. Adsorption on
such centres in medium occurs in the presence of elec-

tron donor's water molecules. Water molecules can
be decomposed and then, influenced by surface fields
and electron excite energy, transferred into a water
molecule. Surface positive core interacts both with
OH^- ions and with water molecules:

(9) $Me^+ + OH^- \rightarrow MeOH$

(10) $2Me - OH \rightarrow Me-O-Me + H_2O$

(11) $Zr^+ + H_2O \rightarrow ZrO^- + H_2$
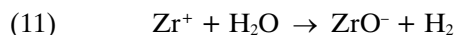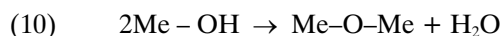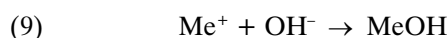
The positive charge on the left side of Eq. (11)
concentrated in oxygen hole ZrO^- on the right side.
Oxygen holes (ZrO^-), formed on 11 surface, can migrate
into the volume due to interacting with volume atoms
of metals.

In order to define the mechanism of such processes,
the influence of preliminary radiation and radiation-
-thermal processing under the different conditions
in the processes of protective and catastrophic oxidation
of zirconium were studied.

Oxidation of pre-treated samples was carried
out under identical conditions at T = 873 K, ρ_{H_2O} =
5 mg/cm³, $\dot{D}$ = 6.18 Gy/s. A radiographic method was
applied to identify the nature of oxide film formed at dif-
ferent stages of thermal and radiation-thermal surface
processes in the Zr + H_2O system and to define defects
regularities in formation processes taking place in the
oxide film influenced by radiation and temperature.
The research on X-ray diffraction of general-purpose
DRON-4 was carried out and diffratographs of the
samples were taken at the following parameters: CuK_α,
Cu – filter, I = 25 mA, V = 35 kV, T = 300 K; inter-
planar spaces in the structure and line intensities were
identified [23, 34]. Line identification in the spectrum
was carried out on [23, 34, 43, ASTM]. At the radiation-
-thermal oxidation of zirconium in contact with water
at first the field-oxide film is formed on the surface.
The system Zr–ZrO_2 with the field-oxide film consists
of α-modification of zirconium, with a hexagonal close-
-packed lattice [14]. In the field of zirconium catastroph-
ic oxidation on the roentgenogram of the system (T =
873 K, ρ_{H_2O} = 5 mg/cm³, τ = 120 min) a line characteristic
for β-modification of zirconium (θ = 26.00; d = 1.77 Å
and θ = 17.83; d = 2.51 Å) was observed. From such
results an assumption can be made that α $\rightarrow$ β transi-
tion occurs at the catastrophic oxidation of zirconium in
contact with water under γ-quantum influence.

The field-oxide film in the initially untreated samples
consists mainly of α-ZrO_2 [14, 23, 28, 34, 43].

The content of defect states of $ZrO_{0.35}$, Zr_3O_{1-x},
Zr_3O in the composition of the treated field-oxide films
is higher than in the untreated samples. Therefore, a
preliminary radiation and radiation-thermal treatment
of zirconium-water contact water, with high radiation
doses, leads to decreased beginning time of catastrophic
oxidation of zirconium. In the initial part of the cata-
strophic oxidation area for zirconium the content of
defect states in the field-oxide film nearly duplicates.

Imperfections in the formed oxide films evoke
the porosity change in Zr–ZrO_2 system [11]. To identify
porosity change regularities for Zr–ZrO_2 system the
specific surface area of the samples at different stages
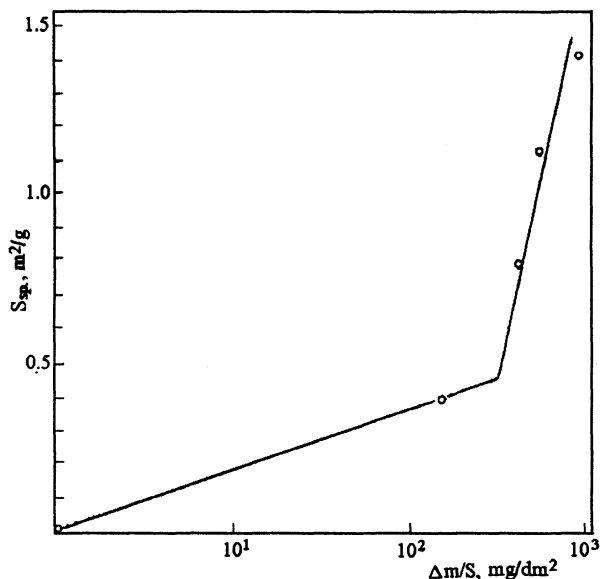
Fig. 8. Dependence of specific surface of Zr–ZrO$_2$ system on the quantity of the oxide phase (in semilogarithmic coordinates) on zirconium surface in radiation-thermal oxidation of Zr in contact with water at T = 873 K, ρ_{H_2O} = 5 mg/cm^3, $\dot{D}$ = 5.98 Gy/s.

of oxidation were studied. The recorded values for the surface area refer to the mass unit of Zr–ZrO$_2$ system. Figure 8 displays the relation of specific surface changes in the Zr–ZrO$_2$ system vs. the quantity of oxide films plotted in semilogarithmic coordinates. As presented, in the dependence on S_{del} = f (Δm/s) two areas can be identified. Namely, area I, which corresponds to forming the field-oxide film, and area II, where catastrophic oxidation of zirconium takes place. As demonstrated, in the area of catastrophic oxidation of zirconium a highly porous oxide film is formed.

Therefore, a conclusion can be made that the existence of defect states in the anion sublattice of oxides shortens the time required for the catastrophic oxidation of zirconium to begin. To attain the decrease of defect states in the anion sublattice of the field-oxide film a radiation treatment of zirconium was carried out in H$_2$O + O$_2$ contact (P_{O_2} = 3 atm, τ = 50 h). As shown in Fig. 9 (curve 1), a preliminary radiation treatment of zirconium in H$_2$O + O$_2$ contact causes zirconium stability to increase towards catastrophic decomposition since in the researched time slot the catastrophic oxidation of zirconium was not observed.
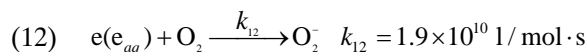
The oxygen present at field oxide film formation due to heterogeneous radiation-chemical decomposition of water and Zr presence causes anion defect states in oxide film to decrease, which protects metal from further oxidation. The oxygen present at radiation-thermal oxidation of zirconium T = 873 K, ρ_{H_2O} = 5 mg/cm^3 in contact with water leads to acceleration of catastrophic oxidation of metal. Still, over a definite time the release of hydrogen was not observed in radiation-thermal oxidation processes of zirconium in contact with water and oxygen. This has evidenced that hydrogen interacts with oxygen at the initial period of radiation-thermal process in contact Zr with water (Fig. 9, curve 1).

Therefore, the presence of oxygen during radiation-thermal oxidation triggers an earlier beginning of catastrophic oxidation (Fig. 8). Oxygen interacts with
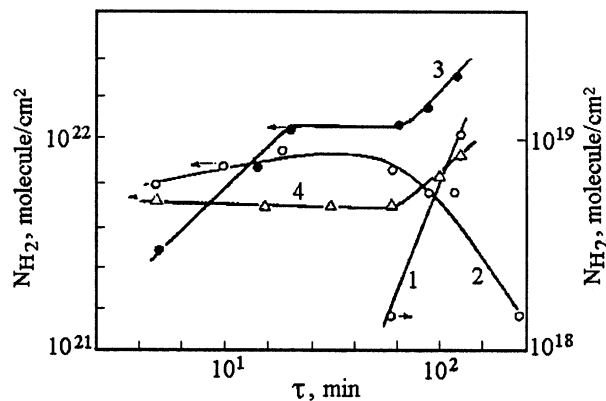
Fig. 9. The influence of oxygen on zirconium oxidation process in the contact with water at T = 873 K, ρ_{H_2O} = 5 mg/cm^3: 1 – samples pre-treated by radiation at T = 300 K, ρ_{H_2O} = 5 mg/cm^3, $\dot{D}$ = 6.18 Gy/s in oxygen medium (P_{O_2} = 3 atm, $\tau_{treatment}$ = 50 h); 2 – oxidation in oxygen presence (P_{O_2} = 3 atm) in contact with water (ρ_{H_2O} = 5 mg/cm^3), T = 873 K, 3 – radiation-thermal processes of oxidation in the initial system of Zr + H$_2$O.

products of water decomposition, as well as with secondary electrons (including solvated electrons).
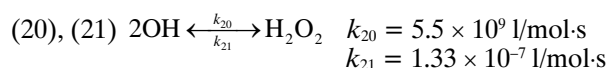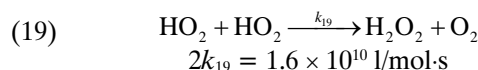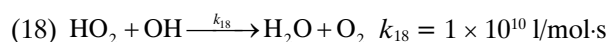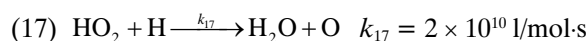
$$(12) \quad e(e_{aq}) + O_2 \xrightarrow{k_{12}} O_2^- \quad k_{12} = 1.9 \times 10^{10} \; 1/\text{mol·s}$$

$$(13) \quad H + O_2 \xrightarrow{k_{13}} HO_2 \quad k_{13} = 2.2 \times 10^{10} \; 1/\text{mol·s}$$

The obtained O$_2^-$ and HO$_2$ are oxidizing and interacting with zirconium surface.

$$(14) \quad Zr^+ + O_2^- \rightarrow ZrO_2$$

$$(15) \quad 2Zr + 2HO_2 \rightarrow 2ZrO_2 + H_2$$

The reactions made the surface to cover with the field oxide film and therefore zirconium samples pre-treated by radiation in the contact with H$_2$O + O$_2$ at T = 300 K show high stability towards further oxidation.

We attempted to explain the observed experimental results regarding the impact of zirconium materials irradiation conditions on the oxidation and accumulation of the end products by applying literature data on water radiolysis with radiolysis products present [1, 6, 8, 9, 11, 15, 19, 24, 27, 30, 31, 35, 37–39, 41, 42]. In the radiation-thermal processes of zirconium oxidation in the contact with H$_2$O + O$_2$ at high temperatures, acceptance of intermediate products of water molecule decays occurs:

$$(16) \quad HO_2 + O_2^- + H_2O \xrightarrow{k_{16}} H_2O_2 + O_2 + OH_{aq}^-$$
$$k_{16} \approx 9.5 \times 10^7 \; 1/\text{mol·s}$$

$$(17) \quad HO_2 + H \xrightarrow{k_{17}} H_2O + O \quad k_{17} = 2 \times 10^{10} \; 1/\text{mol·s}$$

$$(18) \quad HO_2 + OH \xrightarrow{k_{18}} H_2O + O_2 \quad k_{18} = 1 \times 10^{10} \; 1/\text{mol·s}$$

$$(19) \quad HO_2 + HO_2 \xrightarrow{k_{19}} H_2O_2 + O_2$$
$$2k_{19} = 1.6 \times 10^{10} \; 1/\text{mol·s}$$

$$(20), (21) \quad 2OH \underset{k_{21}}{\overset{k_{20}}{\longleftrightarrow}} H_2O_2 \quad k_{20} = 5.5 \times 10^9 \; 1/\text{mol·s}$$
$$k_{21} = 1.33 \times 10^{-7} \; 1/\text{mol·s}$$

(22) $e_{aq}^- + H_2O_2 \xrightarrow{k_{22}} OH^- + \,^\cdot OH$
$k_{22} = 1.2 \times 10^{10}$ l/mol·s

(23), (24) $OH^- + OH \xleftarrow[k_{24}]{k_{23}} O^- + H_2O$
$k_{23} = 1.3 \times 10^{10}$ l/mol·s
$k_{24} = 1.8 \times 10^6$ l/mol·s

(25) $H_2 + OH \xrightarrow{k_{25}} H + H_2O$ $k_{25} = 3.7 \times 10^7$ l/mol·s
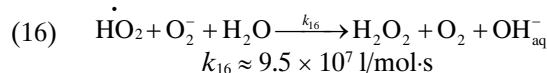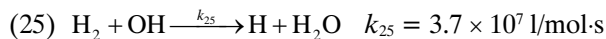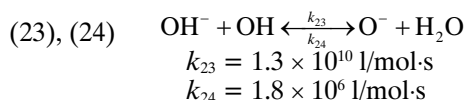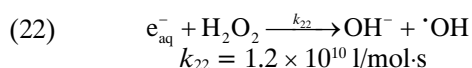
Therefore, in the medium of radiation-thermal oxidation of zirconium with oxygen present, the molecular hydrogen accumulation is not observed (Fig. 10). The accumulation of molecular hydrogen is observed once the oxygen present in the reactionary medium had been consumed. Despite the lack of hydrogen accumulation in the relatively high rated radiation-thermal processes in Zr–H$_2$O–O$_2$ system, that is the evidence of presence of oxidative fragments that are formed following (12)–(25) during zirconium oxidation.

Under real operating conditions at nuclear reactors in order to suppress the accumulation of explosive gas mixture to the coolant, a molecular hydrogen is added. Therefore, the determination of regularities for radiation-thermal processes in contact with molecular hydrogen is of great significance. At the presence of hydrogen after a defined time a hydride phase ZrH$_x$ is formed (Fig. 10, curve 2) and it may undergo hydrolysis in contact with water at the temperature of 875 K.

(26) $ZrH_x + H_2O \rightarrow Zr(OH)H_{1+x}$
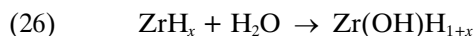
The formation of hydride phase stimulates the increased fragility of zirconium surface, which in turn facilitates further progress of the oxidation process. Therefore, hydrogen presence in a reactionary phase stimulates the acceleration of both protective and catastrophic zirconium oxidation processes.

The acceleration of destructive oxidation processes of zirconium materials under radiation can be explained either by radiation processes of defect formation in Zr–ZrO$_2$ system, or by radiation-thermocatalyst influence of the oxide phase in water decomposition process.

Zirconium oxide displays a high radiation-catalyst activity in water decomposition process, which mainly
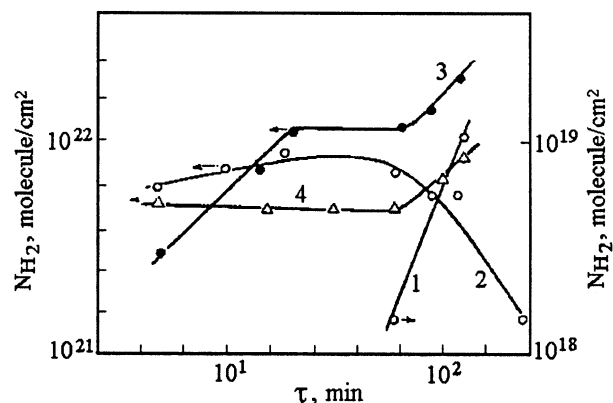
Fig. 10. Kinetics of molecular hydrogen accumulation in radiation-thermal ($\dot{D} = 6.18$ Gy/s) processes at $T = 873$ K, ρ_{H_2O} = 5 mg/cm³: 1 – in the system of Zr + H$_2$O + O$_2$ ($P_{O_2} = 3$ atm); 2 – in the system of Zr + H$_2$O + O$_2$ ($P_{O_2} = 2.5$ atm); 3 – in the initial system Zr + H$_2$O; 4 – pre-treated in O$_2$, $T = 573$ K.

consist in energy transferring with participation of non-equilibrium charge carriers. For zirconium material oxidation at the temperature $T = 873$ K the radiation-chemical yield for molecular hydrogen in heterogeneous radiolysis of water, with ZrO$_2$ present, reaches G (H$_2$) = 8.5 molecule/100 eV [20, 21].

Thereby, the obtained results on radiation-heterogeneous decomposition of water in contact with zirconium materials, allow to formulate the following conclusions:

– The radiation effect in heterogeneous processes of water decomposition is displayed through energy transfer to gas and adsorbed phases.
– The formation of oxide phase on the metal surface stimulates thermo-radiation processes of water decomposition resulting from radiation-catalyst activity of the oxide phase.
– Radiation-heterogenic processes in contact with Zr–H$_2$O and Zr–ZrO$_2$–H$_2$O create conditions for accumulation of additional quantity of hydrogen from coolant in water-cooled nuclear reactors. The results should be taken into account when detailing scenario for both standard and emergency operation mode in water-cooled nuclear reactors.
– Within the influence range of ionizing radiation and temperature in heterogeneous systems Me–H$_2$O, two parallel processes take place. Namely, the formation of oxide film and establishment of defective states.
– At certain concentrations of oxide phase and defective states, catastrophic oxidation of metals occurs.
– In radiation-heterogeneous processes in Me–MeO–H$_2$O contact the radiation effect consist in acceleration of protective oxides and shortening time required to initiate catastrophic metal oxidation.
– Due to radiation-thermal processes in Zr–H$_2$O system a porous oxide phase is formed on the surface, which triggers catastrophic metal oxidation.
– A preliminary radiation-oxidation treatment of zirconium materials increased their stability to radiation-thermal decomposition in contact with coolant.
– Presence of (H$_2$O) H$_2$ and O$_2$ in coolant at temperatures $T \geq 873$ K leads to increased destructive oxidation of zirconium materials in water-cooled nuclear reactors.

The reported results show that radiation and radiation-thermal processes in contact of zirconium materials with water accelerate the formation of molecular hydrogen and metal oxidation both in the area of protective oxide layer formation on the surface and in the destructive oxidation of these materials in contact with steam. The influence of radiation stimulates acceleration of destructive oxidation of zirconium materials in contact with water.

The detected radiation effect in the process of hydrogen accumulation and metal oxidation in contact of zirconium materials with steam at different temperatures can be exploited in radiation material science, and in defining accurate scenarios for nuclear accidents.

The analysis of the accident in Chernobyl, on 26 April 1986, and Fukushima-1 disaster in Japan and resulting damage points to gaseous mixtures as the source of danger for both incidents. They resulted from radiation-thermal processes occurring in the systems

of water-fuel elements and water-decelerator. In both accidents core temperature increased and the materials of fuel elements and the fuel itself melted. Water was supplied in order to cool the reactors and radiation--thermal and thermal processes were initiated. Our results show that at $T > 1073$ K under reactor conditions the catastrophic destruction of metal materials occurs, which resulted in interaction with the formatted water hydrogenous gaseous mixtures.

Considering that in both cases the interaction of coolant with materials of fuel elements occurred under nuclear fission conditions, the contribution of radiation processes resulting from fission radiolysis [28] lead to water concentration higher than in γ-radiolytic processes. Thus, under real accident conditions the destruction rate of the structural materials and hydrogen accumulation can be higher than in the model experiments we observed.

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