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# PRELIMENARY RADIATION-OXDIZING TREATMENT INFLUENCE ON RADIATION-CATALYTIC ACTIVITY OF ZIRCONIUM DURING WATER DECOMPOSITION PROCESS

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Today mainly water-cooled nuclear reactors predominate in atomic energetics. For safe work of nuclear reactors detection of accumulation process of explosives, formed during radiation and temperature influence on heat-carriers in contact with materials of nuclear reactors in normal and emergency regimes of work is of great importance.

The main sources of molecular hydrogen formation in normal and emergency regimes are the processes of liquid and vaporous water in vapometallic reaction [1-5].

At the result of these processes molecular hydrogen concentration in heat-carrier composition always exceeds theoretically expected concentration.

One of the main ways to solve the problem of water-cooled reactors safety is detection of possibilities to raise material resistance of fuel elements and heat carrier to joint action of ionizing radiation and temperature. The second way is inhibition of radiation-catalytic activity of construction materials' surface during the process of water decomposition.

It's been established, that one of the ways to raise resistance of zirconium materials to the influence of ionizing radiation is formation of thin oxide film on the surface of metals.

In the given work the influence of preliminary oxidizing treatment of zirconium surface on its radiation-catalytic activity during the process of water decomposition. With this aim zirconium is exposed to preliminary influence of gamma-quantum in contact with hydrogen peroxide at different meanings of absorbed radiation dose.

## EXPERIMENTAL TECHNIQUE

Investigations were carried out in static conditions in special quartz ampoules with the volume V=1,0 $sm^3$.

Reactor zirconium with 99,9% of purity as thin strap was taken as the investigation object.

Contacting surface of the samples was determined on the base of their geometric size and it made 34,6 $sm^2/g$.

With the aim of exclusion of influence of surface organic pollutions on the process of molecular hydrogen accumulation the samples had been preliminarily purified with the help of organic solvents – ethyl alcohol, acetone, and then were rinsed with distilled water.

After that the samples were dried at the temperature 300÷320K in inert gas medium – argon.

Dried samples were weighted to within $\pm 5\cdot 10^{-5}$ g and were transferred into quartz ampoules. Ampoules with the samples were vacuumized up to P=$10^{-3}$Pa, firstly at the temperature T=300K, and then 473 K.

Then hydrogen peroxide ($C_{H2O2}$=9mole/l) was added to samples until they were wholly covered with it. Ampoules were connected with special gasometer.

The samples were exposed to preliminary radiation influence of gamma-rays ($\dot{D}$ = 1.14$Gy/s$) at different times, then the samples were dried and weighted.

After weighing the samples were transferred to the special ampoule for experiments of radiation-catalytic activity in processes of radiolytic decomposition of water.

Necessary quantity of water was added into ampoule with samples by the way of water vapor condensation from graded volume of vacuum-adsorption plant.

The accuracy of water injection into the ampoule with samples from vacuum-adsorption plant in investigated range of density meanings of water vapor is ±5%.

The temperature during the experiments was maintained to within ±1K.

Radiation and radiation-thermal processes were carried out on isotopic source of γ-излучения $^{60}$Co.

Source dosimetry was carried out by means of chemical dosimeters – ferrosulfate, cyclohexane and methane.

Re-calculation of adsorbed radiation dose meanings in investigated systems was made by comparison of electronic densities [6].

Gas products of the processes were transferred to special graded volumes and were analyzed by gas chromatograph method («Газохром 3101»)

At radiolytic process T=300K in structure of gas products except for $H_2$ observed also $O_2$, and at thermoradiolysis - $H_2$. Zirconium materials' corrosion was investigated by weight method.

For this purpose the initial metal samples and those ones exposed to the experiments dried in vacuum P≈$10^{-5}$Pa were weighted to within $10^{-5}$g.

Materials corrosion at the result of radiation-thermal and thermal processes was characterized according to samples overweight $\Delta m$= $m_i$- $m_0$.

## RESULTS AND THEIR DISCUSSIONS

For the purpose of detection the influence of metal materials on water radiolysis, the kinetics of $H_2$ at radiolytic decomposition of water and water + reactor zirconium system at T=300K had been investigated.

Radiation-chemical outlet G($H_2$) at this made 0,44 and 0,54 molecules/100eV, accordingly.

Observed growth of G($H_2$) meanings during $H_2O$ radiolysis in presence of metal Zr in comparison with radiolysis outlet of pure water may be explained by the contribution of emitted from metal under the influence of γ-quantum δ-electrons and formation of additional active centers of water decomposition on metal surface. The process speed at this makes $\Delta W$=3,5·$10^{13}$ molecules/sec.

In conditions of nuclear reactors work metal constructions are exposed to simultaneous influence of temperature and radiation in contact with heat-carrier.

That's why kinetics of molecular hydrogen accumulation at radiation-thermal ad thermal processes in Zr contact with water at T= 673K and ρ=5 mg/ sm$^3$ and preliminary metal irradiation.

For the purpose of detection the contribution of radiation-heterogenic processes in radiation-thermal heterogenic processes, radiation-thermal and thermal processes of water decomposition were held in identical conditions (T=673K and ρ=5mg/sm$^3$). On the basis of initial linear section of experimental kinetic curve $W_{rt}$($H_2$) and $W_t$($H_2$) speed meanings were determined.

The speed of radiation components $W_r$($H_2$) of radiation-thermal process of hydrogen accumulation was determined from speed difference of radiation-thermal and thermal processes:

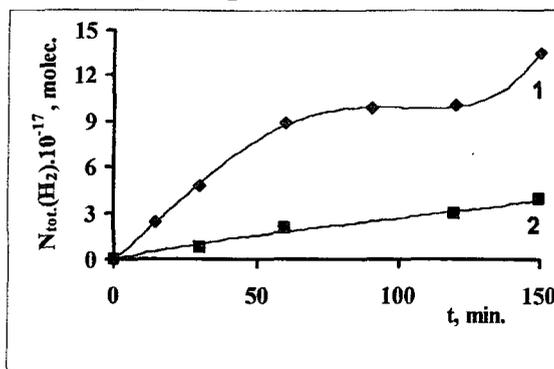$$W_r (H_2) = W_{rt}(H_2) - W_t(H_2)$$

In fig.1 and 2 typical kinetic curves of molecular hydrogen accumulation at thermoradiolysis and thermal processes of water decomposition in presence of metal zirconium

During preliminary radiation-oxidizing treatment of zirconium in presence of $H_2O_2$ formation of oxide film on metal surface may be observed.

$$Zr + H_2O \rightarrow Zr - ZrO_x + H_2O + H_2$$
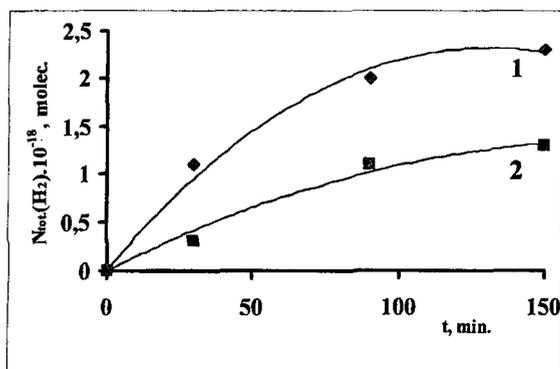


**Fig.1.** Kinetic curves of molecular hydrogen accumulation in radiation-thermal (1) ($\dot{D} = 1.14 Gy/s$) and thermal (2) processes of water decomposition in presence of Zr samples, previously radiationally treated at D=20,52 kGy in presence of $H_2O_2$.

**Fig.2.** Kinetic curves of molecular hydrogen accumulation in radiation-thermal (1) ($\dot{D} = 1.14 Gy/s$) and thermal (2) processes of water decomposition in presence of Zr samples, previously radiationally treated at D=287,28 kGy in presence of $H_2O_2$.

In fig.3 the dependences of radiation-chemical outlet and molecular hydrogen accumulation speed accordingly in radiation-thermal (1) ($\dot{D} = 1.14 Gy/s$) and thermal processes of water decomposition in presence of Zr at T=673K, $\rho$=5mg/sm$^3$ from the time of its preliminary radiation treatment in presence of $H_2O_2$ at T = 300K.

During the first period of treatment thin oxide film appears on the surface, that has high radiation-catalytic activity in water decomposition process.

With the increase of treatment time the thickness of surface oxide film grows and x meaning in Zr-ZrO$_x$ system approaches to 2. That's why radiation-catalytic activity is approximately about the meanings, observed in ZrO$_2$-H$_2$O system.

Formation of the surface oxide film during the preliminary treatment of Zr in presence of $H_2O_2$ during the period $\tau$-30-50 hours (D=123-205 kGy) leads to passivation of the surface in radiation and thermal processes of water decomposition.
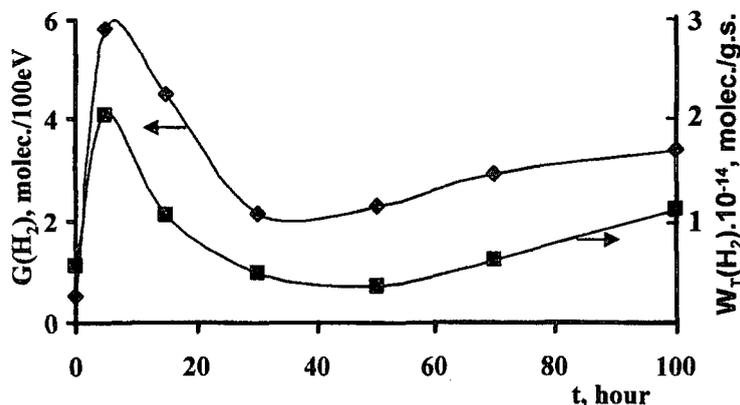


**Fig.3.** Dependences of radiation-chemical outlet and molecular hydrogen accumulation in ($\dot{D} = 1.14 Gy/s$) radiation-thermal (1) and thermal processes (2) of water decomposition at T=673K, $\rho$=5mg/sm$^3$ from the time of preliminary treatment of Zr, in contact with $H_2O_2$ at T = 300K.

During the further increase of the thickness in surfaced oxide film their defectiveness increases as well, what leads to acceleration of catastrophic oxidation of metal phase (Fig.2).

That's why during radiation-thermal processes in presence of samples, previously radiationally treated in presence of $H_2O_2$ at $D \geq 280$ kGy, catastrophic oxidation zone may be observed.

So, on the basis of achieved results the following conclusions can be drawn:

- Radiation-oxidizing treatment of zirconium in presence of $H_2O_2$ at $D=15 \div 25$ kGr leads to increase of surface catalytic activity in water decomposition process.

- Surface states of zirconium, formed during preliminary treatment of Zr in presence of $H_2O_2$ within the limits of adsorbed dose of gamma-irradiation $D=120\text{-}200$ kGy, are characterized by low catalytic activity in the radiation and thermal water decomposition processes.

- Radiation treatment of zirconium in presence $H_2O_2$ at doses $D \geq 280$ kGy leads to increase of catalytic activity in radiation-thermal water decomposition process and acceleration of catastrophic oxidation process of metal.

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