# PRELIMENARY RADIATION -OXDIZING TREATMENT INFLUENCE ON ELECTROPHYSICAL PROPERTIES OF ZIRCONIUM

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The dependences of resistivity (ρ), thermoelectromotive force (α) voltage-current characteristic of thin zirconium film 80÷200 mkm of thick from adsorbed dose of γ-quantum have been investigated. It's been found out that when initial meanings of absorbed dose are insignificant (D≤20kGy) in Zr-$ZrO_2$ system ρ is decreased at the expense of formation of point defects (biographic protective oxide film). The further increase of absorbed dose (up to definite value) leads to radiation-heterogeneous processes of protective oxide film formation with high vacancy concentration that is accompanied with ρ increase.

Fuel element materials of water-cooled nuclear reactors are exposed to simultaneous impact of fission products, ionizing radiation, temperature, water and water radiolysis products [1]. That's why different defects are formed in these materials, their surfaces are oxidized and finally they loose air-tightness that may cause emergency situation.

Among metal materials, applied as heat carriers zirconium and its alloys are of great interest. In order to determine mechanism of processes, passing in zirconium materials, different physicochemical methods are applied.

In the given work the mechanism of oxidation and defect formation processes in zirconium during its preliminary radiation treatment in $H_2O_2$ medium and during further radiation-thermal processes in its contact with water is investigated by means of resistance test, measurement of thermoelectromotive force (α) and current-voltage curve of zirconium films.

## EXPERIMENTAL TECHNIQUE

Reactor zirconium with 99,99% of purity was taken as the investigation object. The samples were previously purified by ethyl alcohol, acetone and distilled water, were dried firstly in air, then in vacuum ($1 \cdot 10^{-3}$ Pa) at T=300K and then T=473K. After that electrophysical parameters of samples were measured. Later on the samples were placed in ampoules with hydrogen peroxide and were exposed to preliminary gamma-rays impact ($\dot{D} = 1.14 Gy/s$) at different exposure times. After that the samples were dried and weighted. After weighting the samples were transferred to special ampoule for radiation-catalytic activity testing in radiolytic water decomposition processes. Necessary water volume was injected into ampoules with samples by water vapors condensation from graded volume of vacuum-adsorption plant. Accuracy of water injection into ampoules with samples from vacuum-adsorption plant in investigated water vapors density limit makes ±5%. Temperature during the experiments was held accurate to ±1K. Radiation and radiation-thermal processes were carried out on isotopic source of γ–radiation $^{60}Co$.

The process gas products were transferred into special graded volumes and analyzed by gas chromatography method («Газохром 3101»). During radiolytic process T=300K besides $H_2$ in gas products composition $O_2$ was observed, and during thermoradiolysis - $H_2$.

Zirconium materials corrosion was investigated by means of weight method. For this purpose initial and exposed to testing metal samples dried in vacuum ($10^{-5}$ Pa) were weighted accurate to $10^{-5}$g. Materials corrosion as a result of radiation-thermal and thermal processes was characterized according to samples overweight $\Delta m = m_i - m_o$.

The impact of zirconium preliminary radiation treatment in $H_2O_2$ medium on electro physical properties has been investigated with the purpose of determination the mechanism of initial

radiation treatment impact on corrosion resistance of zirconium materials. For this purpose after samples treatment the electrical resistivity and thermoelectromotive force. were measured.

Zirconium lamella had the following size: thickness d=0,012÷0,20mm; width b=2,0÷4,0mm; L==20÷25mm.

Measurement of samples resistivity was held with the help of four balloon-born point contacts by compensation method at direct current and by formula $\rho = \frac{1}{\sigma} = \frac{U}{A} \cdot \frac{S}{L}$, where U – voltage drop between two probes (2,3), A-current between probes (1,4), S-sample section. Resistivity inaccuracies didn't exceed 2,7%. The following devices were used: power sources of TEC 41 type, universal voltmeter B7-21 and B7-21A for voltage drop measurement; for current measurement – combined digital device Ц431.

During thermoelectromotive force (α) measurement, the absolute stationary method with compensation was used. Here temperature gradient $\Delta T=2\div3^{\circ}$ was created along the lamella and temperature was measured by differential med-constantan thermocouple and thermo electromotive force was determined by formula $\alpha=\frac{\bar{U}}{\Delta T} \cdot \gamma$, where γ - thermocouple sensitivity [2-5]. During α measurement the inaccuracy made 6,0%.

After that the samples were placed in special ampoule with $H_2O_2$, were connected with gasometer and were exposed to gamma-irradiation impact at different exposure times. Source dosimetry was carried out by chemical dosimeters – ferrosulphate, cyclohexane and methane. Re-calculation of radiation absorbed dose in investigated systems was maintained by comparison of electron densities [6].

After treatment the samples were dried and the measurement of electro physical properties was held in identical conditions.

Corrosion resistance and catalytic activity of previously treated samples was tested in radiation-thermal and thermal processes of water decomposition when T=673K, $\rho(H_2O)$= 5mg/sm$^3$, $\dot{D} = 1.14 Gy/s$, $\tau_{tr}$=30min. And with all this the kinetics of molecular hydrogen accumulation and metal oxidation as a result of radiation-thermal and thermal processes in contact with water had been studied.

## RESULTS AND THEIR DISCUSSION

Made experiments can be grouped in the following way:

I. Radiation-oxidation treatment.

Preliminary radiation treatment of zirconium in contact with 30% $H_2O_2$ solution at different intervals had been carried out.

It's known that dependence of hydrogen peroxide's gamma-radiolytic decomposition speed from concentration of its water solutions passes maximum over the concentration range of hydrogen peroxide $C(H_2O_2) \approx 30\div40\%$ [7].

That's why radiation-oxidation treatment of zirconium was carried out in $H_2O_2$ with 30% of concentration. Under the influence of gamma-quantum as a result of electrons emission and relcase, positive states and coordinated unsaturated atoms are formed accordingly on surface of zirconium.

$$Zr \rightarrow Zr^{+} + Zr - \quad (1)$$

The most possible hydrogen peroxide transformation processes are the following:

$$H_2O_2 \rightarrow 2OH \quad (2)$$

$$OH + H_2O_2 \rightarrow H_3O^{+} + HO_2^{\cdot} \quad (3)$$

$$HO_2 + H_2O \rightarrow H_3O + O_2^- \quad (4)$$

$$H_2O_2 + O^- \rightarrow HO^- + OH + O_2 \quad (5)$$

The process may pass under the influence of surface states of zirconium and decomposition products may interact with the surface:

$$Zr + OH \rightarrow Zr - OH$$

$$Zr + HO_2 \rightarrow Zr - O_2H$$

In both cases hydroxyl groups and partially protonated hydrogen are formed on the surface of zirconium. In such cases samples resistance is decreased due to hydrogen and OH-group existence. That's why depending upon $\rho = f(D)$ during the initial treatment times ($D \leq 20 \cdot 10^3 Gy$) the minimum is observed (fig.1).

During the further decrease of treatment time and accordingly of radiation absorbed dose, radiation dehydroxylation and interaction with other $H_2O_2$ radiolysis products can be observed:

$$Zr - OH \rightarrow Zr - O + H$$

$$Zr^+ + HO^- \rightarrow Zr - OH$$

$$Zr^+ + O_2^- \rightarrow ZrO_2$$

As a result of these reactions, the oxide film that conditions decrease of samples' electrical resistivity is formed on the surface of metal zirconium

During the following radiation dose increase creation of deficient states takes place in surface oxide phase.

As a result of radiation-heterogeneous processes O-holes that migrate inside metal phase are formed in oxide phase. In consequence of these processes electrical resistivity of oxide phase is decreased under the law $\rho = f(D^{-0.8})$.

So, preliminary zirconium treatment in oxidizing medium($H_2O_2$+$H_2O$) under the impact of gamma radiation depending upon absorbed dose meaning leads to metal conductivity decrease and increase.

II. Previously radiation-oxidationally treated samples were exposed to test in radiation-thermal and thermal processes in contact with heat carrier $H_2O$ at T=673K, $\rho(H_2O)$=5mg/sm$^3$, $\dot{D} = 1.14 Gy/s$, $\tau_{tr}$=30min. Then electrophysical properties of tested samples were studied.

Dependences of electrical resistivity of samples that were exposed to radiation-thermal (2) and thermal (3) testings are given in fig.1.

As it's seen during radiation-thermal processes recovery of initial electrophysical state doesn't pass wholly. During these processes in $Zr - ZrO_x - H_2O$ system oxidizing defectformation takes place in oxide phase. Dehydroxylation and oxidation of zirconium surface in radiation-thermal processes pass with higher speed, than in thermal processes. That's why during thermal processes recovery of highoxide state takes place in samples, treated during longer times $\tau$=50h, $\tau$=30h. Electrical resistivity of samples after radiation-thermal and thermal processes is lower than in initial ones that may indicate high concentration of defect states in them. That's why in samples, previously exposed to radiation-oxidizing treatment at D≥200kGy, in radiation-thermal processes during longer intervals of contact catastrophic oxidation area is observed ($\tau_{cat.} \geq$120min).

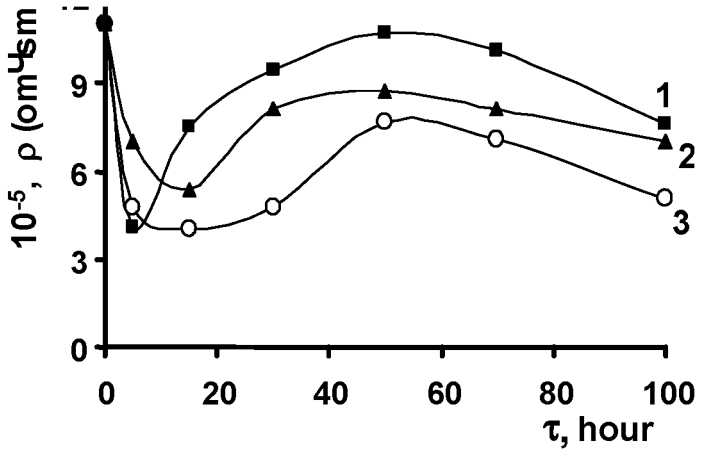


**Fig.1.** Dependence of electrical resistivity of zirconium samples, previously irradiated at T=300K (1), thermally (2) and radiation-thermally (3) treated at T=700K ($\tau_{tr.}$=0,5 h).

In fig.2 presents the dependences of relative resistivity change $\frac{\Delta\rho}{\rho}$ and thermoelectromotive force (α) of radiation-thermally treated lamellas from radiation absorbed dose. As it is seen from the figure $\frac{\Delta\rho}{\rho}$ at little doses grows intensively, but at comparatively high doses (D≥ $3{,}5\cdot10^3$ Gy) growth of $\frac{\Delta\rho}{\rho}$ subsides and slowly approaches to saturation. In this area thermoelectromotive force (α) meaning begins to subside in consequence with ρ change, but at low doses of α within the limits of experiment inaccuracy doesn't almost change and is equal to $(6\div8)\frac{mkv}{grad}$.

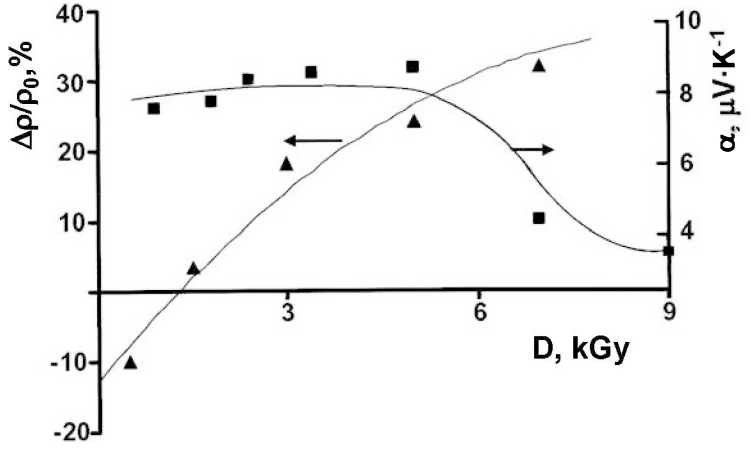


**Fig.2**. Dependence of $\frac{\Delta\rho}{\rho_0} = f(D)$ and $\alpha=f(D)$ for metal zirconium (Zr) from absorbed dose.

Resistivity change ρ depending upon the preliminary radiation treatment may be divided into four areas (fig1):

1. When absorbed dose meaning is D=(0÷20)·$10^3$Gy. ρ is abruptly decreased on 50%
2. When: D=(20÷35)·$10^3$Gy ρ meanings are increased.
3. When D=(50÷70)·$10^3$Gy – saturation range begins.

4. When $D>70\cdot10^3$Gy ρ meanings again subside slowly.

Similarly ρ meanings change for thermally and radiation-thermally treated samples. This is evidently connected with appearance of first point defects. In area $D=(20\div35)\cdot10^3$Gr increase of ρ is connected with the fact that in parallel with point defects, vacancies begin to appear and to increase due to migration of internodal atoms. The fact itself that $\rho\sim m^*\cdot n^{-1}$ and $\alpha\sim m^{*3/2}\cdot n^{-1}$ means that here not only point defects, but vacancies, the concentration of which increase also are of great importance. This in its turn affects efficient masses of current carriers $m^*$ [5]. In area $D=(20\div35)\cdot10^3$Gy ρ passes saturation range , where these two competing concentrations even. Originated vacancies come to zirconium surface and in interaction with water interact with oxygen. As a result of interaction Zr-$ZrO_2$ is formed, localization of which passes up to the moment when the surface becomes saturated with them. Comparative resistivity in samples after radiation-thermal treatment grows slowly (fig.2), but thermo electromotive force meanings decrease. As it is known thermo electromotive force (α) is very sensitive to metal Fermi-surface properties change and so on surface layer, that had a contact with water the process passes very difficult. Here not only abovementioned two factors but also appearance of different bubbles, and also generation of different point defects and their recombination are of great importance.

Basing upon abovementioned factors in processes that pass in concrete area of zirconium surface in contact with water, it's necessary to evaluate surface chemisorption processes, though these processes at low absorbed doses of γ-quantum are not very significant. But we are interested in surface changes of electrophysical properties. These properties to a greater or lesser extent are sensitive to adsorption processes that pass on zirconium surface. For qualitative evaluation on the base of current-voltage curve electrical resistivity (R) for all groups was determined: previously irradiated, radiation-thermally and thermally treated after preliminary treatment.

The meanings of comparative electrical resistivity $\frac{\Delta R}{R_0}$ were determined and comparative resistivity $\frac{\Delta\rho}{\rho}$ changes were compared. Within the limits of experiment inaccuracy they coincided. Nevertheless at large absorbed doses ($D>60\cdot10^3$Gr) change of $\frac{\Delta\rho}{\rho}$ meanings for radiation-thermally treated samples is 2,4 times as much, than for thermally treated ones. It's explained by the fact that at definite doses the relation of comparative resistivities of thermally treated $\frac{\Delta\rho'}{\rho'}$ and previously irradiated $\frac{\Delta\rho}{\rho}$ samples makes $\left(\frac{\Delta\rho'}{\rho'}\right)\Big/\left(\frac{\Delta\rho}{\rho}\right)=\frac{0.15}{0.08}=1.88$, but at corresponding radiation doses for radiation-thermally treated samples this relation makes $\left(\frac{\Delta\rho''}{\rho''}\right)\Big/\left(\frac{\Delta\rho}{\rho}\right)=\frac{0.36}{0.08}=4.5$.

So, the following results are received from the experiment:

1. At small doses in Zr-$ZrO_2$ system defect states and free $O^-$ holes are formed in oxide layers.
2. During the following radiation dose increase, the radiation-heterogeneous formation of protective oxide layer that conditions ρ resistivity increase of samples up to definite dose takes place

**REFERENCES**

1. Solntsev Yu.P. Radiattsyonnostoikie materialy, M. Energoizdat, 1993.
2. J. Zaiman. Fizika metallov, T.1, 1972.
3. Duglas D. Metallovedenie tsirkonia, M: 1975.

4. Bakai A.S. "Structure and Radiation Damage of Metallic Glasses" Usnehi fiziki metallov ANU 2002, T.3 No1. C. 87-106
5. Gorbachev, Spitsyna. "Fizika poluprovodnikov i metallov", M: 1985
6. Pikaev A.K. Dozimetria v radiatsionnoi himii. M.: Nauka, 1975, p.11.
7. Pshezhetskii S.Ya., Mechanizm radiatsionno-himicheskih reaktsii. Izdatel'stvo Himiya, Moskva, 1968, p.168