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# INFLUENCE OF PRE-RADIATION-OXIDIZING TREATMENT ON THE SPECIFIC RESISTANCE OF ZIRCONIUM

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***Abstract:*** The effect of preliminary radiation-oxidative treatment on the relative change in the resistance ($\Delta\rho/\Delta\rho_0$) of metallic zirconium has been studied. The contribution of preliminary radiation-oxidative treatment to the change in the electro physical characteristics during thermal and radiation-thermal tests in the contact of zirconium with water is revealed.

***Keywords:*** radiation-oxidative, metallic zirconium, radiation-thermal, γ-quanta.

## 1. Introduction

As can be seen from the literature data, radiation-heterogeneous processes in contact with preliminarily radiation-oxidative treated zirconium with water cause a change in the amount of surface oxide film. The formation of an oxide film, in turn, changes the radiation-catalytic activity and physicochemical properties, which affect the kinetic parameters. One of them, the most sensitive is the electro physical and optical properties of metal surfaces. Therefore, after testing zirconium samples in the process of water decomposition, the study of the electro physical and optical properties is of great interest [1-6].

The study of the kinetics of radiation, radiation-thermal and thermal processes shows that in metals used directly in a nuclear reactor, there is not only a change in natural defect states but also the appearance of new defects - displaced interstitial atoms, as well as a change in surface properties due to adsorption, insertion other substances (for example $O_2$, $H_2$), corrosion, etc.

As is known, the accumulation of point defects and impurities introduced during irradiation (for example, $O_2$, $H_2$) strongly affects the physical properties of the metal. Thus, a consistent study of the physical properties before and after thermal and radiation-thermal treatment makes it possible to judge changes in electronic and structural defects and draw certain conclusions about the processes taking place.

The purpose of this work is to change the resistance and thermo EMF. metallic zirconium, occurring in samples pretreated and tested under conditions of radiation-thermal and thermal effects.

## 2. Experimental

Investigated plates of reactor zirconium (purity 99.99%) with a thickness of d = 0.012 - 0.20 mm; width b = 2.0 - 4.0 mm and length l = 20 - 25 mm. The samples were preliminarily cleaned with ethyl alcohol, acetone, and distilled water, dried first in the air, then in vacuum ($1 \cdot 10\text{-}3$ Pa) at T = 300K, and then at T = 473K. Then the samples were placed in ampoules with 30% - solution of hydrogen peroxide ($CH_2O_2$ = 9 mol/L) and subjected to preliminary exposure to gamma rays (absorbed dose rate D = 1.14 Gy/s) at different exposure times. Then the samples were dried and their electro physical parameters were measured. Then the samples were placed in

special ampoules to test their radiation-catalytic activity in the processes of radiolysis decomposition of water. The required amount of water was introduced into ampoules with samples by condensation of water vapor from a graduated volume of a vacuum adsorption unit. The accuracy of introducing water into ampoules with samples from a vacuum adsorption installation in the investigated range of water vapor density values was ± 5%. During the experiments, the temperature was maintained with an accuracy of ± 10C. Radiation-oxidative treatment and radiation-thermal tests were carried out on an isotope source of γ-radiation $^{60}Co$. Dosimetry of the source was carried out with chemical dosimeters - ferrosulfate, cyclohexane, and methane.

The electrophysical properties of samples subjected to preliminary radiation-oxidative treatment were also determined under conditions of radiation-thermal and thermal tests in contact with a coolant - water (density d = 5 mg/cm$^3$) at T = 673K, D = 1.14 Gy/s. The kinetics of radiation decomposition of hydrogen peroxide in aqueous solutions has been studied in many works. Some of the dependencies established in them are consistent with each other. At the same time, there are some discrepancies. In [5, 7-8], the kinetics of the reaction of radiation decomposition of hydrogen peroxide under the action of излучения-radiation in the concentration range 0.5-18 mol $\cdot L^{-1}$ was investigated. At concentrations up to 4 mol $\cdot L^{-1}$, the reaction was first order with concerning hydrogen peroxide; at concentrations above 4 mol$\cdot$ $L^{-1}$, the reaction order is higher. The reaction rate is proportional to the square root of the radiation intensity; the activation energy is 5.1 kcal$\cdot$mol$^{-1}$.

## 3. Results and discussion

The paper presents the results of a study of changes in the electrophysical properties of preliminarily radiation-oxidatively treated zirconium samples as a result of their testing during thermo- and thermoradiolytic processes of water decomposition. At the same time, special attention is paid to the following aspects;

- ✓ During the operation of radiation-oxidatively treated zirconium samples under real operating conditions of water-cooled nuclear reactors, all parameters of these samples change, including surface physicochemical parameters, corrosion resistance, and electrical properties. A special place in the change of these properties belongs to the processes of defect formation in the Zr-$ZrO_x$ system.
  The study of changes in the electrophysical properties of pretreated zirconium samples allows us to judge the mechanism of defect formation and, ultimately, about all radiation-heterogeneous processes in the Zr-$ZrO_x$-$H_2O$ system. Therefore, we have carried out studies of changes in resistivity-, thermo emf-of preliminarily radiation-oxidatively treated zirconium samples after testing them in contact with water at T = 673K, at various absorbed doses.
- ✓ The current-voltage characteristics of these samples were studied to clarify the state and quantitative features of charge carriers formed in the Zr-$ZrO_2$ system under the influence of radiation-heterogeneous processes in contact with water.

Based on the experimental results, generalizations are made about the mechanism of defect formation and their effect on the electrophysical properties of the Zr-$ZrO_2$ system.

When irradiated with γ-quanta, which creates damage in metals and alloys, complex processes occur that lead to the formation of defect structures in the form of electronic and lattice defects, pores, precipitates, etc. This is the reason for the application of the method of resistivity and thermoelectric power [9]. Publications in recent years indicate increased attention to this

method, due to its high sensitivity to smaller defect structures and in solving many problems in damage physics and radiation materials science.

In the present work, are investigating the possibilities of methods for studying the resistivity ($\Delta\rho/\Delta\rho0$) and thermo-emf ($\alpha$) in the study of the processes of radiation oxidation of the surface of zirconium in contact with $H_2O_2$. During the radiation-oxidative treatment of metals, an oxide phase is formed on the surface, which affects the resistivity of materials. Therefore, electrophysical methods began to be widely used as a method for obtaining information on the state of structural materials in nuclear technologies.

The figure shows the dependences of the resistivity of preliminarily radiation-oxidatively treated samples on the time of γ-irradiation . As can be seen from the figure, at low values of the absorbed dose D≤20kGy, the resistivity of the samples decreases in comparison with the initial state. The observed decrease in the resistivity in the initial regions of the time of radiation-oxidative treatment of zirconium is associated with surface radiation-heterogeneous processes. When irradiated with γ-quanta, which creates damage in metals and alloys, complex processes occur that lead to the formation of defect structures in the form of electronic and lattice defects, pores, precipitates, etc. This is the reason for the application of the method of resistivity and thermo-emf [9]. Publications in recent years indicate increased attention to this method, due to its high sensitivity to smaller defect structures and in solving many problems in damage physics and radiation materials science.

In the present work, the possibilities of methods for studying the resistivity ($\Delta\rho/\Delta\rho0$) and thermo-emf are investigated. In the study of the processes of radiation oxidation of the surface of zirconium in contact with $H_2O_2$. During the radiation-oxidative treatment of metals, an oxide phase is formed on the surface, which affects the resistivity of materials. Therefore, electrophysical methods began to be widely used as a method of obtaining information on the state of structural materials of nuclear technologies.

The figure shows the dependences of the resistivity of preliminarily radiation-oxidatively treated samples on the time of γ-irradiation at. As can be seen from the figure, at small values of the absorbed dose D≤20kGy, the resistivity of the samples decreases compared to the initial state. The observed decrease in the resistivity in the initial regions of the time of radiation-oxidative treatment of zirconium is associated with surface radiation-heterogeneous processes. In the initial doses of radiation-oxidative treatment of zirconium, there is an accumulation of defect states in the surface oxide phase:

$$Zr\text{-}ZrO_x \xrightarrow{\sim} Zr \cdot ZrO^*$$

where - Zr-ZrOx is the initial state of the surface with a protective oxide phase, $Zr \cdot ZrO^*$ is the defect state formed as a result of the action of γ-quanta (the defect state can be attributed to the localized state of nonequilibrium charge carriers, vacancies of anions, surface O- holes) .

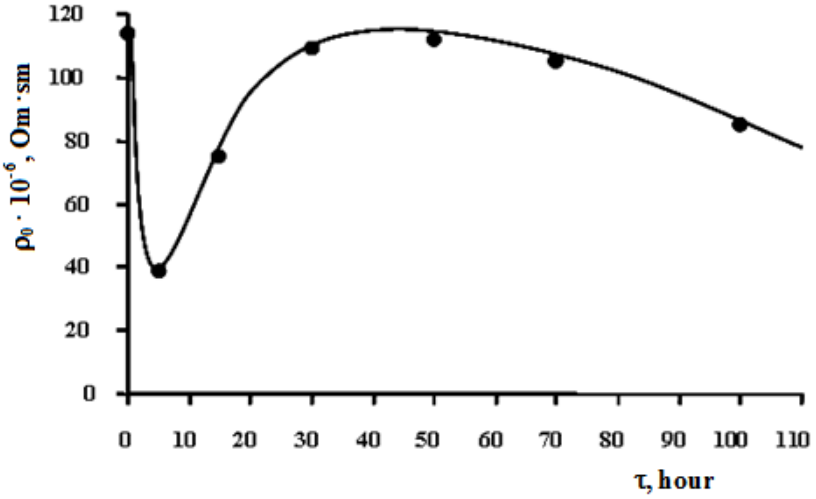


*Fig. Dependence of the resistivity of zirconium samples on the time of preliminary irradiation at T = 300K, D=1.14 Gy/s in an $H_2O_2$ medium.*

As a result of the interaction of surface defect states with the products of $H_2O_2$ radiolysis, hydroxyl-containing states of zirconium atoms are formed and dissolved in the contacting medium. Partial destruction of the biographical oxide film and the formation of charged states lead to a decrease in the resistivity of the metal. With a further increase in the time of radiation-oxidative treatment, an oxide film is formed. As a result of the interaction of charged and coordination-unsaturated metal atoms by the products of $H_2O_2$ radiolysis, a new oxygen-containing state of the zirconium surface is formed.

After D≥123 kGy, the predominance of the formation of the oxide phase begins during radiation-heterogeneous processes in the Zr-$H_2O_2$ system, therefore, the resistivity of the radiation-oxidatively treated samples begins to increase.

The obtained results show that a stable protective oxide film can be formed in a certain amount on the zirconium surface. Its properties depend on the methods of its formation. It was revealed that a stable state of a protective oxide film is formed on the surface of zirconium during radiation-oxidative treatment. The stability of the surface oxide state remains in the range of values of the absorbed radiation dose D≈123 ÷ 290 kGy. The observed decrease in the resistivity of the samples preliminarily radiation-oxidatively treated in an $H_2O_2$ medium in the region of the absorbed radiation dose D≥290 kGy is associated with the accumulation of stable charged states in the Zr-ZrOx system.

To elucidate the nature of the dependence of the resistivity ρ(τ) on the preliminary oxidative treatment of the metal surface, the relative change in the resistance and thermo emf of the samples preliminarily radiation-oxidatively treated at times corresponding to a minimum (5 hours) was studied.

## 4. Conclusion

The completion of the protective oxide film during the radiation-oxidative treatment of zirconium (D≥80 kGy) is accompanied by a decrease in electrical conductivity and current values in the study of their current-voltage characteristics. When these samples are tested in the processes of radiation-thermal and thermal decomposition of water, partial destruction of the protective oxide film occurs as a result of which additional charge carriers accumulate on the

surface. The rate of destruction of the surface oxide film and the accumulation of charge carriers during radiation-thermal processes are higher than during thermal processes.

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## ВЛИЯНИЕ ПРЕДВАРИТЕЛЬНОЙ РАДИАЦИОНО-ОКИСЛИТЕЛЬНОЙ ОБРАБОТКИ НА УДЕЛЬНОЕ СОПРОТИВЛЕНИЯ ЦИРКОНИЯ


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***Резюме:*** Изучено влияние предварительной радиационно-окислительной обработки на относительно изменения сопротивления ($\Delta\rho/\Delta\rho_0$) металлического циркония. Выявлен вклад предварительной радиационно-окислительной обработки в изменение электрофизических характеристик при термических и радиационно-термических испытаниях в контакте циркония с водой.



***Ключевые слова:*** радиационно-окислительной обработки, металлический цирконий, радиационно-термические, γ-кванты.


## QABAQCADAN RADİASİYA-OKSİDLƏŞDİRİCİ İŞLƏMƏNİN ZİRKONİUMUN XÜSUSİ MÜQAVİMƏTİNƏ TƏSİRİ


**T.N. Ağayev, G.T. İmanova, S.Z. Melikova, A.Q. Əliyev**



***Xülasə:*** Qabaqcadan radiasiya-oksidləşdirici işləmənin metal zirkoniumun xüsusi müqavimətinin nisbi ($\Delta\rho/\Delta\rho0$) dəyişməsinə təsiri öyrənilmişdir. Zirkoniumun su ilə gedən termiki və radiasiya-termiki proseslərdə elektrofiziki xassələrinin dəyişməsinə ilkin radiasiya-oksidləşdirici işləmənin payı aşkar edilmişdir.



***Key words:*** radiasiya-oksidləşdirici işlənmə, metal zirkonium, radiasiya-termiki, γ-kvantları.