INFLUENCE OF GAMMA-RADIATION ON THE HYDROGEN YIELD AT WATER RADIOLYSIS ON THE SURFACE OF NANO-ZIRCONIUM

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The kinetics of accumulation of molecular hydrogen at a water radiolysis on the surface of nano-zirconium at the room temperature is investigated. The contribution of radiation processes at interaction of nano-zirconium with water is revealed and rates of production and value of a radiation-chemical yield of molecular hydrogen are determined. It is studied radiation and heterogeneous decomposition of water by method of IR-spectroscopy. It is shown that adsorption of water in nano-zirconium happens on the molecular and dissociative mechanism.

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INTRODUCTION

Zirconium – belong to number of rare metals which owing to exclusive properties is widely applied in nuclear power, radio electronics and in some other branches of the science. Due to the development of nuclear power zirconium has drawn to itself attention as possible constructional material for power nuclear reactors. It has caused the organization of industrial production of malleable zirconium and alloys on its basis. Zirconium value as constructional material for atomic science and technology is defined by the fact that zirconium has the small section of capture of thermal neutrons (0.2 b), high anticorrosive resistance, good mechanical properties [1–12].

Lately, the analysis of literary data indicates that in nuclear reactors with water coolant radiolysis processes in water in a liquid and steam state as a source of molecular hydrogen and also vapor-metallic reaction are considered. Radio lytic processes of accumulation of hydrogen in reactors are characterized by an yield of molecular hydrogen which were observed at a homogeneous radiolysis of water at which influence of radiation and radiation and thermal processes in contact of constructional materials with water on accumulation of molecular hydrogen wasn't considered [10, 14].

As a result of superficial physical and chemical processes of metal materials with hostile environment the condition of a surface which finally leads to oxidation of these materials [7–8, 14] changes. In this work the kinetics of accumulation of molecular hydrogen at a heterogeneous radiolysis of water in nano-Zr+H_2O_{vap} and nano-Zr+H_2O_{liq} systems is investigated at the room temperature.

EXPERIMENTAL PART

Heterogeneous radiolysis of water carried out in static conditions in special quartz ampoules. The quantity of nano-Zr in ampoules was about $4\cdot10^{-2}$g. It was taken double distilled water for researches. Water into ampoules was entered by two methods. In the first case water from a steam state was adsorbed (H_2Os) on a surface of nano-Zr at $T = 77$ K. The amount of the entered water in ampoules corresponded to density of vapors of water in ampoules, at $\rho = 5$ mg/сm^3. In the studied intervals of temperatures, there is a balance between an amount of water in the steam and adsorbed state. In the second case, water from calibration volume was entered into ampoules to a full covering of a nano-Zr sample by liquid water with the mass of $m_{liq} = 0.2$g. Then ampoules with samples cooled to 77 K and soldered.

Radiation and radiation and thermal processes carried out on a ^{60}Co isotope source. Power of the absorbed dose of gamma radiation was determined by chemical – ferro-sulphatic, cyclohexane and methane dosimeters [13]. The analysis of products of radiation and heterogeneous processes was carried out on the Agilent-7890 gas-chromatograph.

By the method of Fourier IR spectroscopy has studied radiation and heterogeneous decomposition of water on a surface of nano-Zr, at a temperature of 300 K. By an X-ray phase method it is established that the used sample exists in two crystal modifications:

– α-Zr – with a hexagonal lattice like magnesium (a = 3.231 Ǻ; with = 5.148 Ǻ; z = 2; spatial P63/mmc group),

– β-Zr– with the cubic volume aligned lattice (a = 3.61 Ǻ; z = 2; spatial Im3m group).

It is shown that adsorption of water in nano-zirconium happens on the molecular and dissociative mechanism. Intermediate products of radiation and heterogeneous decomposition of water are registered: an ion - radicals of molecular oxygen, hydrogen peroxide, hydride of zirconium and hydroxyl groups.

The comparative analysis of change of absorption bands of molecular water and surface hydroxyl groups depending on temperature is carried out and also the stimulating role of radiation in radiation and thermal process of water decomposition is revealed. Fourier IR spectrums of absorption registered on the FTIR spectrometer Varian 640 IR in the range of frequencies $\nu = 4000…400$ cm^{-1} in case of indoor temperature. For registration of absorption spectra, tablets 50…100 μm thick were pressed from the Zr nanopowders. IR spectrums of samples are registered in special quartz cells with windows made of CaF_2, which allowing getting the spectra of the adsorbed water, decomposed under action of γ-radiation.

RESULTS AND DISCUSSIONS

The kinetics of accumulation of molecular hydrogen at a heterogeneous radiolysis of water in nano-Zr+H_2O liq and nano-Zr+H_2O vap systems is studied. Nano-Zr as constructional material has radiation firmness and working capacity in nuclear reactors. The radiation and catalytic activity nano-Zr is defined by two methods as it has been specified in an experimental part. In fig. 1 the kinetic curves of molecular hydrogen accumulation at a heterogeneous radiolysis of water are given in the presence of nano-Zr in two states. From initial linear parts of kinetic curves, values of accumulation rates and a radiation-chemical yield of hydrogen in the studied systems are defined.

On the kinetic curve shown in Fig. 1,a it is possible to allocate two sites:

I – area which is characterized by rather high rate of accumulation of hydrogen on initial line sections;

II – rather slow stage of accumulation of molecular hydrogen.

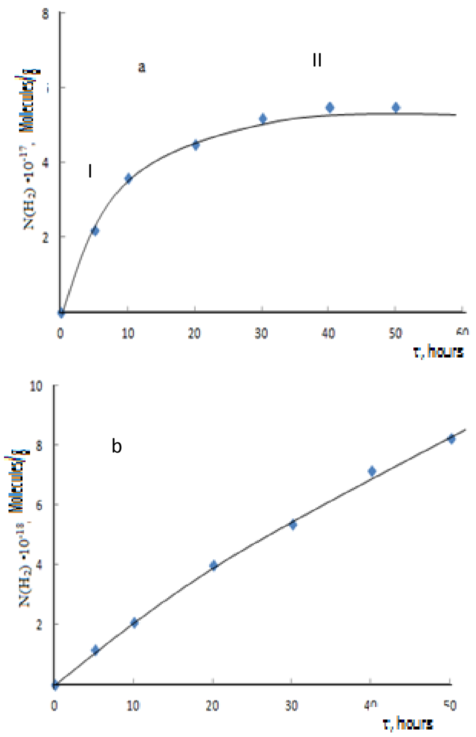

Fig. 1. A kinetic curves of molecular hydrogen formation at radiation and heterogeneous decomposition of water in nano-Zr+H_2O_{liq} (a) and nano-Zr+H_2O_{vap} (b) systems at T=300 K, D=0.15 Gy/s

On the kinetic curve shown in Fig. 1,b it is possible to consider growth of accumulation rate of molecular hydrogen. It once again demonstrates that covered completely with water a catalyst layer in the reactor, in the process of decomposition of water not only the energy carriers received on the basis of zonal transitions, but also δ-electrons with small energy and the emitted electrons participate. Therefore, finally a hydrogen yield in nano-Zr+H_2O_{liq} is more, than in nano-Zr+H_2O_{vap}. From the table it is visible that at a heterogeneous radiolysis of water in a condition of a full covering of a layer of nano-zirconium (nano-Zr+H_2O_{liq}), observed values of a radiation-chemical yield of hydrogen in ~5.4 times are more, than at a heterogeneous radiolysis of water in the adsorbed state on the surface of nano-zirconium. It demonstrates that in case of nano-zirconium in volume of water, there is an effective transfer of energy from a solid phase to water molecules. The second slow stage of a radiolysis, existing on kinetic curves demonstrates that there is a diffusion complicated stage of a heterogeneous radiolysis of water in the presence of nano-zirconium at *T*=300 K. Influences of temperature on accumulation rates of molecular hydrogen at a heterogeneous radiolysis of water are studied on the example of the nano-Zr+H_2Os systems as temperature increasing in nano-Zr+H_2O_{liq} system in the closed ampoules is experimentally impossible.

Values of accumulation rates and radiation-chemical yields of molecular hydrogen at a radiation and heterogeneous radiolysis of water in two states at *T* = 300K

No	Irradiated systems	$W(H_2)$, molecules·g^{-1} s^{-1}	$G(H_2)$, molecules/100eV
1	Zr+H_2O_{ads}	$1.22 \cdot 10^{13}$	1.3
2	Zr+H_2O_{liq}	$6.67 \cdot 10^{13}$	7.1

Radiation decomposition of water in the nano-Zr system it is studied by Fourier's IR-spectroscopy method. In Fig. 2 (curve 1), the IR spectrum in nano-Zr system after γ-radiation, nano-Zr+H_2O (water vapors) system is shown at the absorbed doses 3 кGy (a curve 2), 20 кGy (a curve 3) and 30 кGy (a curve 4). Apparently from the Fig. 2 (a curve 1), a surface of nano-Zr, undergone thermal vacuum processing - clean as in it there are no absorption bands (AB) caused by both water availability, and hydrocarbon pollution.

Irradiation of nano-Zr+H_2O_{vap} heterosystem by γ-quanta at the absorbed dose 3 kGy and at the room temperature (*T* = 300 K), is followed by emergence of a number of AB in spectral area ν=3800…400 cm^{-1} (a curve 2). In low-frequency area ν=800…400 cm^{-1} the AB with a maximum at 670 cm^{-1} is found. According to [15], the AB at 670 cm^{-1} belongs to valent fluctuation of Zr–O bond that indicates formation of an oxide film on a nano-Zr surface contacting with water vapors. With increase in a dose of absorption (from 3 to 30 кGy), the tendency of increase in intensity and expansion of a AB of the Zr–O bond is observed. Observed changes specify that to increase in the absorbed dose there is growth of thickness of an oxide layer and formation of Zr–ZrO nanostructure.

Irradiation of the nano-Zr-ZrO+H_2O heterosystem by γ-quanta with an absorption dose 3 kGy at the room temperature, leads to formation of new AB in the area 1000…800 cm^{-1} with maxima at 1020 and 970 cm^{-1}. According to [16], AB at 1020 cm^{-1} it is caused by adsorption of molecular oxygen – a product of decomposition of vapors of water on the surface of zirconium and points to formation of an oxygen radical ion in him π-form, i.e. π-O_2. At observation of AB in this sample at 970 cm^{-1}, it is visible that she is caused by formation of twice deployed hydrogen peroxide of O_2^{2-} [16].

Thus, Fourier IR-spectroscopy allows registering intermediate products of radiation decomposition of water in nano-Zr-ZrO+H_2O heterosystem. Surface hydrides of zirconium are most interesting among these products. So, since 3 kGy in a range ν = 2000…1800 cm^{-1}, there are AB with maxima at

1992 and 1880 cm^{-1} which intensity are redistributed with increase in values of the absorbed dose. These AB belong to valent fluctuation of Zr-H and indicate on formation of surface hydrides of zirconium – the ZrH and ZrH_2 types among which ZrH_2 is considered as the most stable form [17].

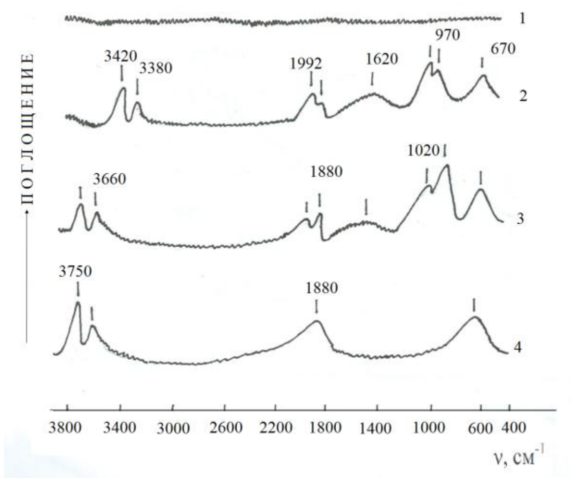

Fig. 2. Fourier IR spectrums of initial nano-Zr (1) and nano-Zr+H_2O_{vap} system at various absorbed radiation doses – 3 kGy (2), 20 kGy (3) and 30 kGy (4)

Thus, Fourier IR-spectroscopy allows registering intermediate products of radiation decomposition of water in nano-Zr-ZrO+H_2O heterosystem. Surface hydrides of zirconium are most interesting among these products. So, since 3 kGy in a range $\nu = 2000…1800$ cm^{-1}, there are AB with maxima at 1992 and 1880 cm^{-1} which intensity are redistributed with increase in values of the absorbed dose. These AB belong to valent fluctuation of Zr-H and indicate on formation of surface hydrides of zirconium – the ZrH and ZrH_2 types among which ZrH_2 is considered as the most stable form [17].

Changes in area of valent fluctuations of hydroxyl (OH) groups, caused by radiation decomposition of water in the heterogeneous nano-Zr+H_2O system, are presented in Fig. 2 (curves 2-4). In Fourier IR spectrums of absorption of nano-Zr samples with the adsorbed water, in the field of valent fluctuations of OH-groups and water ($\nu = 4000…3000$ $см^{-1}$), bands of the hydrogen-connected group with a maximum of 3420 cm^{-1} and also the adsorbed water molecule at 3380 cm^{-1} are observed (Fig. 2, a curve 2). Wide AB with a maximum of 1620 cm^{-1}, is also shown in the field of deformation fluctuation of molecular water. With growth of value of the absorbed dose in ranges, the AB of molecular water and the hydrogen-connected hydroxyl group decreases (a curve 3) and disappears (a curve 4). So, increase in the absorbed dose from 3 to 30 кGy is followed by full and partial disintegration of molecular water and formation of isolated OH – groups (a curve 3–4). Isolated OH groups are shown at 3660 and 3750 cm^{-1} which belong to isolated OH-groups of I type (3750 cm^{-1}) and three coordinated bridges of III type (AB at 3690 cm^{-1}) [10–11].

In Fig. 3 Fourier IR spectrums of initial nano-Zr (1) and nano-Zr+H_2O_{liq} system are presented at various absorbed radiation doses – 3 kGy (2), 20 kGy (3), 30 kGy (4) respectively. Apparently from the drawing, radiation of system leads to formation of an oxide film on a surface of nano-Zr (valent fluctuation of Zr–O bond at 670 cm^{-1}).

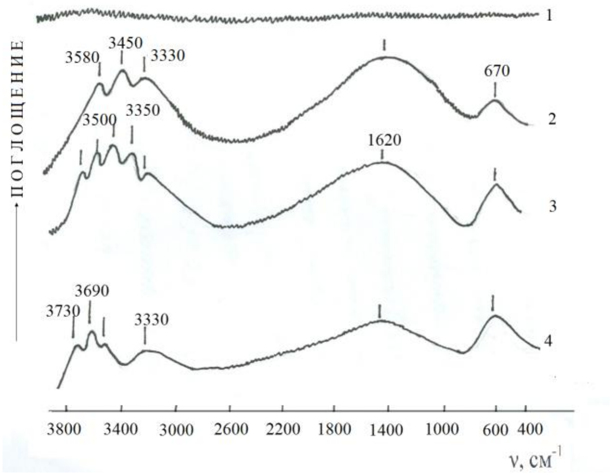

Fig. 3. Fourier IR spectrums of initial nano - Zr (1) and nano-Zr+H_2O_{liq} system at various absorbed radiation doses – 3 kGy (2), 20 kGy (3) and 30 kGy (4)

In a range there is a wide asymmetric band ($\nu_{1/2} = 850$ cm^{-1}) at the absorbed dose 3kGy with the center of gravity of 1620 cm^{-1}. This band belongs to deformation fluctuation of OH-group of molecular water (a curve 2). In the field of valent fluctuations, molecular water is shown at 3280 cm^{-1}. With growth of the absorbed dose, AB order with a maximum at 1620 cm^{-1} is narrowed in ~ 1.2 times, its intensity decreases in ~ 2 times (curves 2–4). At the same time there is a partial decomposition of molecular water (3300 cm^{-1}) and H – connected OH-groups (3550, 3450, 3580 cm^{-1}) and also formation of isolated OH – groups (3730, 3690 cm^{-1}).

The comparative analysis of Fourier IR - spectrums of absorption of nano-Zr+H_2O_{vap} and nano-Zr+H_2O_{liq} heterosystems shows that in both cases, radiation decomposition of water molecules is followed by formation of an oxide film on the surface of zirconium. In the first case it is possible to find and register AB of intermediate and active products, an ion – radical groups π-O_2-and O_2^{2-}, and also surface hydrides.

In nano-Zr+H_2O_{vap} heterosystem full ecomposition of water molecules, and in nano-Zr+H_2O_{liq} system – partial decomposition of water occurs.

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ВЛИЯНИЕ ГАММА-ИЗЛУЧЕНИЯ НА ВЫХОД ВОДОРОДА ПРИ РАДИОЛИЗЕ ВОДЫ НА ПОВЕРХНОСТИ НАНОЦИРКОНИЯ

Т.Н. Агаев, А.А. Гарибов, В.И. Гусеинов

Исследована кинетика накопления молекулярного водорода при радиолизе воды на поверхности наноциркония при комнатной температуре. Выявлен вклад радиационных процессов при взаимодействии наноциркония с водой и определены скорости образования и значения радиационно-химического выхода молекулярного водорода. Методом ИК-спектроскопии изучено радиационно-гетерогенное разложение воды. Показано, что адсорбция воды в наноцирконии происходит по молекулярному и диссоциативному механизмам.

ВПЛИВ ГАММА-ВИПРОМІНЮВАННЯ НА ВИХІД ВОДНЮ ПРИ РАДІОЛІЗІ ВОДИ НА ПОВЕРХНІ НАНОЦИРКОНІЮ

Т.Н. Агаєв, А.А. Гарібов, В.І. Гусеінов

Досліджено кінетику накопичення молекулярного водню при радіолізі води на поверхні наноцирконію при кімнатній температурі. Виявлено внесок радіаційних процесів при взаємодії наноцирконію з водою і визначені швидкості утворення і значення радіаційно-хімічного виходу молекулярного водню. Методом ІЧ-спектроскопії вивчено радіаційно-гетерогенне розкладання води. Показано, що адсорбція води в наноцирконії відбувається за молекулярним і дисоціативним механізмами.