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RESEARCH OF RADIATION-THERMAL WATER DECOMPOSITION ON NANO-Zr

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Abstract: Using IR-Fourier spectroscopy, the radiation-thermal decomposition of water in nano-Zr was studied in the temperature range 300–673K. It has been shown that water adsorption in nano-zirconium occurs by molecular and dissociative mechanisms. Intermediate products of radiation-heterogeneous decomposition of water were registered: radical ion of molecular oxygen, zirconium hydride, and hydroxyl groups. A comparative analysis of the change in the IR absorption bands of H_2 and surface OH groups with temperature has been carried out and the stimulating role of radiation in the radiation-thermal process of water decomposition has been revealed. The rate of formation and the radiation-chemical yield of molecular hydrogen G (H_2) is determined to depend on the process temperature.

Keywords: nano-Zr, γ-radiation, IR spectra

1. Introduction

It is known that nanosized metal zirconium powders are used as various technological products. One such product is fuel cells, which serve as a converter of thermal energy into an electric cell. Besides, zirconium is one of such structural materials that have radiation resistance and operability in nuclear reactors [1-8].

In connection with the development of nuclear energy, zirconium has attracted to itself the taking out as a possible structural material for nuclear power reactors. The value of zirconium as a structural material for nuclear science and technology is determined by the fact that it has a small thermal neutron capture cross-section (0.2 bar), high anti-corrosion resistance, and good mechanical properties. The larger these values, the larger the neutrons the material absorbs and the more it impedes the development of a valuable reaction.

Naturally, materials with minimal capture-cross sections are selected for the reaction zone of reactors [8]. Thus, zirconium has a very small capture cross-section of thermal neutrons. Therefore, metallic zirconium does not contain impurities, and its alloys are used in nuclear energy for the manufacture of fuel elements (fuel elements), fuel assemblies, and other structural materials.

This paper presents the results of Fourier-IR-spectroscopic studies of the radiation-thermal decomposition of water in a heterogeneous system of nano-Zr-H_2O at temperatures T = 300–673K and exposure to γ-quanta in order to establish the role of intermediate particles and to reveal the patterns of adsorption-active hydroxyl groups in these processes.

2. Experimental technique

Nano-Zr nanopowders with particle sizes d = 75 nm were used as the object of study. Before adsorption, the zirconium samples were subjected to thermal vacuum treatment at T = 673K and a pressure of 10^{-3} Pa for 12 hours to remove organic impurities and dehydroxylate the

surface. The surface cleanliness was controlled by the intensity of the bands in the IR spectra caused by water and hydrocarbon contamination. FT-IR spectra were recorded on a Varian 640 IR FT-IR spectrometer in the frequency range ν = 4000-400 cm^{-1} at room temperature. To record the absorption spectra from Zr nanopowders, tablets 50–100 μm thick were pressed. The IR spectra of the samples were taken in a special quartz cell with CaF_2 windows, which made it possible to obtain spectra of adsorbed water decomposed by temperature and radiation. When overlapping bands related to various forms of adsorbed water, the total contour was decomposed into individual components according to the procedure [8].

Double-distilled water served as an adsorbate, from which extraneous gases were removed by repeated freezing in a trap with liquid nitrogen, followed by pumping. The adsorption of water vapor was studied by the method [5]. Radiation-thermal and thermal decomposition of water in the nano-Zr + H_2O system was carried out at T = 300–673K. Samples were irradiated on a ^{60}Co isotope source with a dose rate of dD_γ/dt = 0.30 Gy/s. Dosimetry of the source was carried out using chemical dosimeters — ferrosulfate and methane methods [9]. Recalculation of the absorbed radiation dose in the studied systems was carried out by comparing the electron densities.

The irradiation time was τ=5.5 hours, (D_γ=5.94kGy).

3. The discussion of the results

The thermal and radiation decomposition of water in the nanocirconium system was studied by IR spectroscopy. The IR spectrum of the initial nano-Zr is shown in Fig. 1. (curve 1), after water adsorption (nano-Zr + H_2O) - curve 2. Then, γ-irradiation of the nano-Zr + H_2O systems was performed at a dose of D = 5.94 kGy and T = 300K (curve 3), T = 473K (curve 4) and T = 673K (curve 5). As can be seen from Fig. 1. (curve 1), the surface of nano-Zr, which has undergone thermal vacuum treatment, is clean, since there are no absorption bands (AB) due to both the presence of water and hydrocarbon contamination. However, in the spectra in the frequency range ν = 900–400 cm^{-1}, very weak ABs with maxima at 745 and a doublet of 490 and 410 cm^{-1} are detected. According to [5], the bands at 745 and 490 cm^{-1} are related to asymmetric Zr-O-Zr and stretching Zr-O vibrations, respectively. With an increase in temperature from 300 to 673 K, there is a tendency to increase the intensity of the absorption bands of Zr-O and Zr-O-Zr bonds. The observed changes indicate that an increase in temperature leads to an increase in the thickness of the oxide layer and the formation of the Zr-ZrO_2 nanostructure. In an unirradiated heterosystem, after water adsorption on the surface of nano-Zr-ZrO_2 in the region of stretching vibrations of hydroxyl (OH) groups, ABs appear, which indicates the occurrence of molecular and dissociative adsorption: the molecular form is adsorption (zirconium band with a maximum at 3275 cm^{-1}) and dissociative chemisorption (relatively narrow bands of 3582 and 3446 cm^{-1}) (Fig. 1, curve 2). The occurrence of two types of adsorption is also confirmed by the formation of AB in the region of OH deformation vibrations with maxima at 1630 and 1610 cm^{-1}. Irradiation of the heterosystem with nano-Zr + H_2O gamma quanta at room temperature (T = 300 K) is accompanied by the appearance of new ABs in the region of 1000–800 cm^{-1} with maxima of 1080 and 1010 cm^{-1}.

According to [10], these bands are associated with the adsorption of molecular oxygen, a product of the decomposition of water on the surface of zirconium dioxide, and indicate the formation of oxygen radical ions in its π-form, i.e. π^-. With increasing temperatures to 473 K (Fig. 1, curve 4), IR from other products of water radiolysis is observed in the IR spectrum. The observed ABs in these samples at 960 and 910 cm^{-1} are apparently due to the formation of doubly dissociated hydrogen peroxide [10–11]. With an increase in temperature from 473 to 673

K, the intensities of these bands decrease, and they completely disappear from the spectrum at 673 K. Thus, Fourier IR spectroscopy makes it possible to detect surface intermediate products of radiation-thermal decomposition of water in a nano-Zr-ZrO_2 + H_2O heterosystem. Among these products, surface zirconium hydrides are of particular interest. Beginning at T = 373 K, in the spectrum in the region of 2000–1700 cm^{-1}, ABs appear with maxima at 1995 and 1880 cm^{-1}, the intensities of which redistribute with increasing temperature. These ABs are related to the stretching vibration of Zr-H and indicate the formation of surface zirconium hydrides of the Zr-H and ZrH_2 type [4-7].

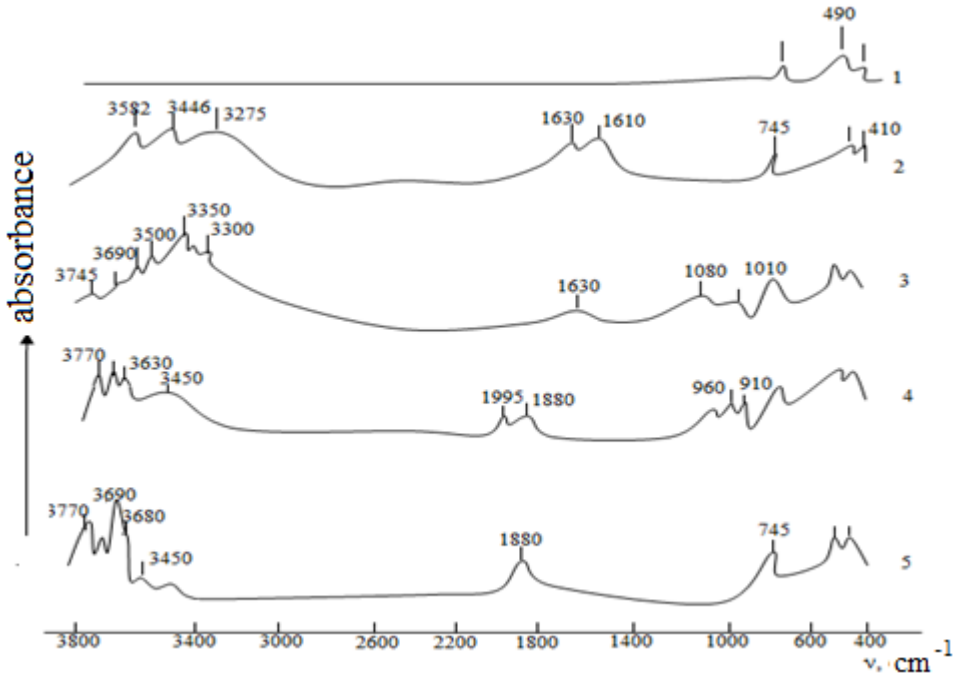

Fig. 1. Fourier IR spectra of nano-Zr treated at 673K (1), before and after exposure γ-radiation to the nano-Zr + H_2O system at 300 (3), 473 (4) and 673 (5)

The changes in the region of stretching vibrations of hydroxyl (OH) groups associated with the radiation-thermal decomposition of water in the heterogeneous system of nano-Zr-ZrO_2 + H_2O are shown in Fig. 1. In the Fourier IR absorption spectra of samples with adsorbed water, in the region of stretching vibrations of OH groups and water (ν = 4000-3000 cm^{-1}), AB hydrogen-bonded groups are observed with maxima of 3580 and 3450 cm^{-1}, as well as adsorbed molecules water at 3275 cm^{-1} (Fig. 1, curve 2).

Radiation-thermal decomposition of water at room temperature is accompanied by a decrease in the intensity of the molecular water band, the formation of a number of AB-linked hydroxyl groups at 3300, 3350, and 3500 cm^{-1}, as well as new bands at 3630 and 3690 cm^{-1}. An increase in temperature to 473 K decreases the intensity of the H-linked bands and increases the bands of isolated OH groups at 3630 and 3690 cm^{-1}. An increase to 673K is accompanied by a complete decomposition of molecular water and partial decomposition of H-linked OH groups (curves 3-5). At T = 473 K, new bands appear at the IR spectrum at 3745 and 3770 cm^{-1}. According to [12–13], the observed - new ABs correspond to isolated hydroxyl groups of I type (AB 3770 cm^{-1}), II type (AB 3745 cm^{-1}) and III type (AB 3630 and 3690 cm^{-1}).

Changes in the intensities of the molecular weight AB, H-bonded and isolated OH-groups at a fixed dose of radiation, depending on the temperature of the process of radiation-thermal

decomposition of water, show that there are antibatical relationships between us (Fig. 2, curves 1, 2, 3). Thus, an increase in temperature from 300 to 673K is accompanied by the complete and partial decomposition of molecular water and H-linked OH groups, respectively, and the formation of isolated OH groups.

This leads to a decrease in the intensities of the H-bonded, and vice versa to an increase in isolated OH-groups.

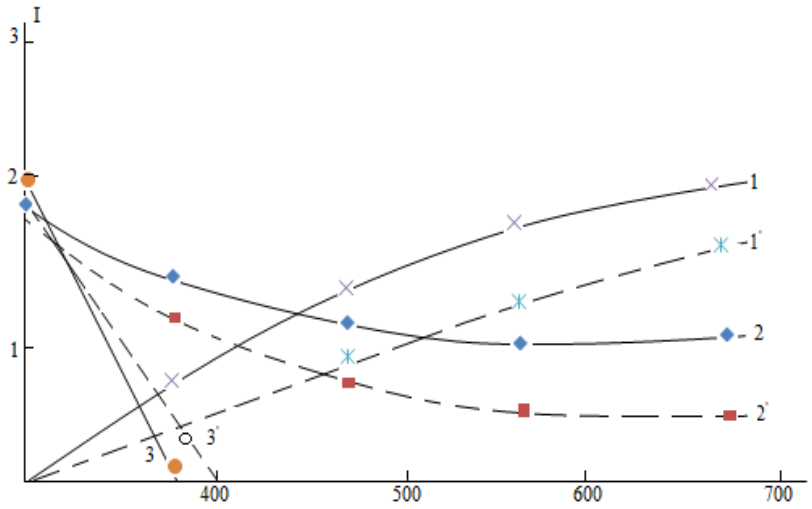

Fig. 2. Dependences of the intensities of the bands of isolated (1, 1′), hydrogen-bonded (2, 2′) surface OH groups and adsorbed water molecules (3, 3′) on the temperature of radiation-thermal (1-3) and thermal processes (1′ -3′) decomposition of water in the heterogeneous system of nano-Zr + H_2O (dashed lines show the dependences for the thermal process (D = 5.94 kGy, τ = 5.5 hours).

Similar changes in the spectra of the nano-Zr-ZrO_2 + H_2O heterosystem are also observed during the thermal process of water decomposition (Fig. 2, curves 1 ', 2', 3 ').

However, in contrast to the radiation-thermal process in the IR spectra during the thermal decomposition of H_2O, the intensities of the molecular weight AB, H-linked, and isolated OH groups turn out to be weak. This indicates the stimulating role of radiation in the process of radiation-thermal decomposition of water in the nano-Zr-ZrO_2 + H_2O heterosystem in the range 300–673K.

The table shows the rates of formation of molecular hydrogen (H_2), the final product of radiation-thermal (W_{RT} (H_2)) and thermal decomposition (W_T (H_2)) water, depending on the process temperature.

Table. The values of the rates and radiation-chemical yields of molecular hydrogen during radiation-thermal, thermal and radiation decomposition of water in the nano-Zr + H_2O system at various temperatures

T, K	***$W_{RT}(H_2)$, molecul/g·s***	***$W_T(H_2)$, molecul/g·s***	***$W_R(H_2)$, molecul/g·s***	***$G(H_2)$, molecul./100eV***
300	-	-	$1{,}22\cdot10^{13}$	1,3
373	$4{,}1\cdot10^{13}$	$2{,}6\cdot10^{13}$	$1{,}5\cdot10^{13}$	2,1
473	$5{,}56\cdot10^{13}$	$2{,}77\cdot10^{13}$	$2{,}79\cdot10^{13}$	3,7
573	$8{,}88\cdot10^{13}$	$5{,}00\cdot10^{13}$	$3{,}88\cdot10^{13}$	5,17
673	$1{,}33\cdot10^{14}$	$0{,}70\cdot10^{14}$	$0{,}63\cdot10^{14}$	8,4

As can be seen from the table, the values of W_{RT} (H_2) are significantly higher than the values of W_T (H_2), which once again confirms the stimulating role of radiation in the radiation-thermal decomposition of water.

4. Conclusion

The possibility of applying the method of Fourier IR spectroscopy for radiation processes in a heterogeneous system of nano-Zr + H_2O in the temperature range T = 300–673 K under the influence of gamma quanta is shown. The molecular and dissociative mechanism of water adsorption was revealed. It was established that, in contrast to the homogeneous phase of water radiolysis in the presence of nano-zirconium, the formation of intermediate decomposition products is accompanied: oxygen-containing radical ions, surface Zr hydrides, and hydroxyl groups. The rates of formation and radiation-chemical yields of molecular hydrogen (H_2) were determined and calculated, and, based on a comparative analysis, the stimulating role of radiation in the radiation-thermal decomposition of water was revealed.

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ИССЛЕДОВАНИЕ РАДИАЦИОННО-ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ ВОДЫ НА ПОВЕРХНОСТИ НАНО-Zr

В.И. Гусейнов

Резюме: Методом ИК-Фурье-спектроскопии изучено радиационно-термическое разложение воды в нано-Zr в интервале температур T=300-673K. Показано, что адсорбция воды в нано-цирконии происходит по молекулярным и диссоциативным механизмам. Зарегистрированы промежуточные продукты радиационно-гетерогенного разложения воды: ион-радикалы молекулярного кислорода, гидрид циркония и гидроксильные группы. Проведен сравнительный анализ изменения ИК-полос поглощения H_2 и поверхностных ОН-групп от температуры и выявлена стимулирующая роль радиации в радиационном-термическом процессе разложения воды. Определены скорость образования и радиационно-химический выход молекулярного водорода $G(H_2)$ в зависимости от температуры процесса.

Ключевые слова: нано-Zr, γ- излучения, ИК- спектры

NANO-Zr-un SƏTHİNDƏ SUYUN RADİASİYA-TERMİKİ PARÇALANMASININ TƏDQİQİ

V.İ. Hüseynov

Xülasə: Furye-İQ-spektroskopiya metodu ilə T=300-673K temperatur intervalnda nano-Zr-da suyun radiasiya-termiki parçalanması tədqiq olunmuşdur. Müəyyən olunmuşdur ki, nano-Zr-da suyun adsorbsiyasi molekulyar və dissosiativ mexanizmlərlə baş verir. Suyun radiasiya-heterogen parçalanmasının aralıq məhsulları qeydə alınmışdır: molekulyar oksigenin ion-radikalları, sirkonium hidridi və hidroksil qruplar. Hidrogenin və səthi hidroksil qruplarının İQ-udulma zolaqlarının müqayisəli analizi aparılmışdır və suyun parçalanmasının radiasiya-heterogen prosesində radiasiyanın stimullaşdırıcı rolu aşkar edilmişdir. Prosesin temperaturundan asılı olaraq molekulyar hidrogenin radiasiya kimyəvi çıxımının və əmələ gəlmə sürətinin qiymətləri hesablanmışdır.

Açar sözlər: nano-Zr, γ-şüalanma, İQ-spektr