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# INVESTIGATION OF OXIDE LAYER FORMATION ON THE SURFACE OF RADIATION-THERMALLY TREATED BERYLLIUM

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***Abstract:*** The kinetics of formation of molecular hydrogen of radiation-thermally treated metallic beryllium in contact with water during thermal and radiation-thermal processes at the temperature range T=573÷673K has been studied. The formation rates and radiation-chemical yields $G(H_2)$ of molecular hydrogen are calculated. It was revealed that the radiation-chemical yield of hydrogen $G(H_2)$ increases from 13.6 to 22.1 molecules/100 eV in the studied temperature range (T=573÷673K). The values of the electromotive force (emf), relative changes in the surface of the oxide layer of radiation-thermal treated beryllium at a temperature of T=673K are calculated, and dependences on the irradiation time are plotted.

***Keywords:*** Beryllium, gamma rays, oxide layer, hydrogen accumulation, electromotive force

## 1. Introduction

Beryllium and its compounds are widely used in atomic and nuclear energy, military equipment, device manufacturing industry, laser technology and other fields. As a result of the impact of ionizing rays and temperature on these substances, changes occur inside and on the surface of the substance [1-3]. The study of these changes is of scientific and practical importance. Beryllium and its compounds are considered to be one of the widely used materials in nuclear energy as a protector and regulator. Since beryllium and its alloys are the subject of extensive research, various research works have been carried out with these substances, but the physical and physico-chemical processes on the surface of these objects have not been studied to the end. The vast majority of modern research and power reactors are water-cooled, and the detection of regularities of radiation-thermal and thermal processes in contact of beryllium metal with water is of great importance from the point of view of both radiation material science and reactor safety. A large number of national and international projects are being implemented in this field, destruction of beryllium and its alloys in the reactor environment, corrosion swelling, etc. problems arising from processes have always been the subject of discussion. Because beryllium mainly interacts with the neutron flood in the reactor environment, researchers have mainly focused on the effect of neutron beams on the durability of beryllium. However, materials inside the reactor vessel are exposed to neutrons and other radiation, including gamma rays. In the emergency mode of the reactors, the beryllium material is exposed to the combined effects of gamma rays and temperature in contact with water. Therefore, the study of processes under the influence of gamma rays and temperature in contact of beryllium material with water is of great scientific and practical importance.

In the presented article, the kinetics of the oxidation of the metal as a result of radiation-thermal processes in contact with water and molecular hydrogen in the temperature interval

T=573÷673K in the radiation-thermal processes were studied.

## 2. Methods of the experiment

Metallic beryllium samples measuring 4x20 mm, reactor material, were used as research objects. In order to eliminate the effect of organic pollution on the surface in the process of hydrogen collection, the samples were pre-cleaned with organic solvents - ethyl alcohol, acetone, and then with distilled water. This operation was repeated three times. Then the samples were dried at a temperature of 300 ÷ 320 K in an inert gas environment and at the same time in a deaerated environment. In the vacuum-adsorption device, 3 special traps cooled by liquid nitrogen are installed in the system to eliminate oil and lubricants falling onto the samples. After that, thermovacuum processing of the samples was carried out in quartz ampoules at a pressure of $P=10^{-3}$ Pa and a temperature interval of T=573÷673 K for 2 hours. Then the samples were cooled to room temperature. The weight of the dried samples was measured with an accuracy of $10^{-5}$ g and placed in quartz ampoules. Radiation and radiation-thermal processes were studied on the isotope source of gamma quanta $^{60}Co$, with a dose rate of $dD_\gamma/dt$ =0,26 Gy/s.

## 3. Results and discussion

In the presented work, the metal oxidation as a result of radiation-thermal processes in contact with water and the kinetics of obtaining molecular hydrogen in radiation-thermal processes in the T=573÷673K temperature range were studied. Under the influence of gamma rays, the oxidation of the metal and the accumulation of molecular hydrogen in the contact medium were observed when beryllium was in contact with water:

$$Be + H_2O \rightarrow BeO + H_2 \qquad (1)$$

Kinetics of hydrogen formation as a result of radiation-thermal and thermal processes at temperatures T=573÷673K under the influence of gamma rays in the Be+$H_2O$ system was studied. The kinetic curves are shown in figure 1. As can be seen from the kinetic curves, the hydrogen formation reaction of Be in contact with water at temperatures T=573÷673K takes place both thermally and radiation-thermally [5,7-9].

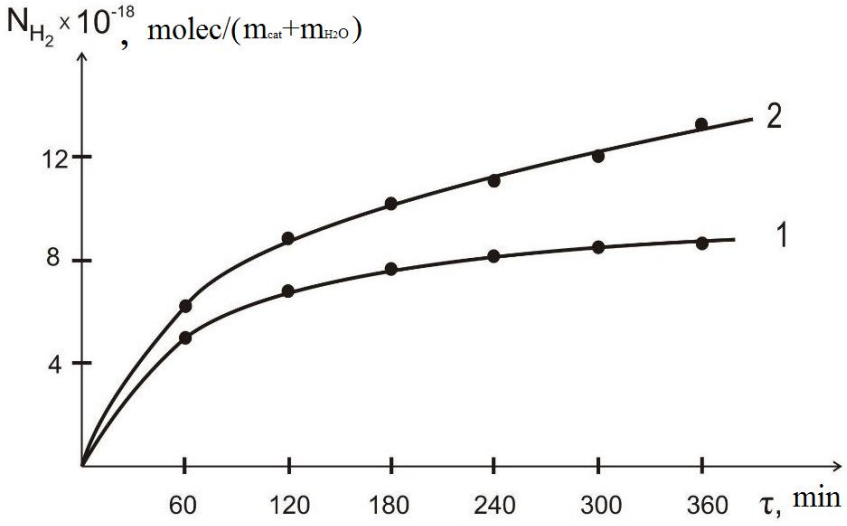


*Fig 1. Kinetics of formation of molecular hydrogen in radiation-thermal (1) and thermal (2) processes during radiolysis of metallic beryllium with water, T=673K, $\rho_{H2O}$=5 mg/cm$^3$, $D_\gamma$=0.26 Gy/sec.*

At temperatures T≥573K, two regions are observed in the kinetic curves - a initial region (high-speed) τ≤80 min and a second region (slow-speed) τ≥100 min.

These results show that beryllium atoms on the surface of the beryllium metallic sample in the initial state undergo rapid radiation-thermal and thermal interaction with water, an oxide layer is formed on the surface. At low temperatures, this layer prevents further interaction. Therefore, in the second part, the oxidation process turns into a slow and fast process.

In the Be-$H_2O$ heterogeneous system, the rate of formation of molecular hydrogen in radiation-thermal processes and the radiation-chemical yield were calculated (table 1).

**Table 1**

The rate of formation of molecular hydrogen in the radiation-thermal processes in the Be-$H_2O$ heterogeneous system and the radiation-chemical yield of hydrogen

| T, K | $W_{RT}$ ($H_2$) *molecule/g·s* | $W_T$ ($H_2$) *molecule/g·s* | G($H_2$) *molecule/100eV* |
|---|---|---|---|
| 573 | $1{,}11\cdot10^{15}$ | $0{,}86\cdot10^{15}$ | 13,6 |
| 673 | $1{,}75\cdot10^{15}$ | $1{,}39\cdot10^{15}$ | 22,1 |

As can be seen from the table, an increase in temperature up to 573÷673 K in radiation-thermal processes leads to a 1.6 times increase in the values of W($H_2$) and G($H_2$).

The graph of the dependence of the relative change of electrical resistance (ΔR/R) and thermal emf on the duration of gamma radiation at the temperature T=673 K is given in figure 2. As can be seen from the graph, at small doses of γ-irradiation, in other words, at short times of irradiation, a protective oxide layer is quickly formed on the surface, which sharply increases the relative change of electrical resistance[10,11].

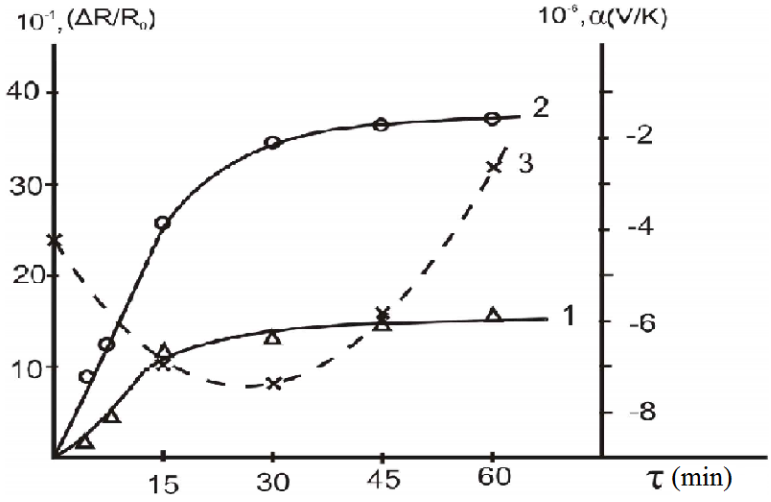


*Fig. 2. Dependence of the relative change of the surface resistance (ΔR/R ) and thermo emf (α) of the beryllium sample on the irradiation time, (T=673 K).1- after thermal treatment; 2-after radiation-thermal treatment; 3- dependence of thermoelectric power after radiation-thermal treatment on τ-irradiation time*

The subsequent increase in the radiation-thermal operation time reduces the effect on the relative change of the resulting resistance and approaches its saturation state. Most likely,

chemical and physical adsorption processes complement each other in the formation of this complex oxide layer. This has little effect on the subsequent change in the resistance of the initially formed protective layer [4,6].

As can be seen from the graph, the relative change of resistance increases rapidly during the initial times of radiation-thermal processing ($\tau<30$ minutes). At large values of the working time ($\tau>30$ minutes), the increase in the $\Delta R/R$ ratio decreases and occurs in both cases. This is an indicator of the resistance of the adsorbed oxide layer formed on the metal surface.

The appearance and formation of an oxide layer in the $Be+H_2O$ system under the influence of gamma rays was confirmed by the Atomic Force Microscope (AFM) method. Thus, in order to detect changes in the morphological dynamics of the surface, three-dimensional surface images of primary and radiation-thermally oxidized beryllium samples were obtained in AFM, histograms of these images were constructed according to dimensions, and Fourier spectra of the surface were drawn. AFM studies have shown that thin oxide layers and nanostructuring process occur on the surface as a result of radiation-thermal modification of the surface relief, depending on the temperature and irradiation time [12].

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## ИССЛЕДОВАНИЯ ФОРМИРОВАНИЯ ОКСИДНОГО СЛОЯ НА ПОВЕРХНОСТИ РАДИАЦИОННО-ТЕРМИЧЕСКИ ОБРАБОТАННОГО БЕРИЛЛИЯ

**Т.Н. Агаев, Ф.Н. Нурмамедова**

***Резюме:*** Исследовано кинетика образования молекулярного водорода радиационно-термически обработанного металлического бериллия в контакте с водой при термическом и радиационно-термическом процессе при интервале температур T=573÷673K. Вычислены скорости образования и радиационно-химические выходы $G(H_2)$ молекулярного водорода. Выявлено, что радиационно-химический выход водорода $G(H_2)$ увеличивается от 13,6 до 22,1 молекул/100эВ в исследуемом интервале температур (T=573÷673K). Вычислена значения электродвижущей силы (э.д.с.), относительные изменения поверхности оксидного слоя радиационно-термического обработанного бериллия при температуре T=673K и построены зависимости от времени облучения.

***Ключевые слова:*** бериллий, гамма излучения, оксидный слой, накопление водорода, электродвижущая сила

## RADİASIYA-TERMİKİ İŞLƏNMƏYƏ MƏRUZ QALMIŞ BERİLLİUMUN SƏTHİNDƏ OKSİD TƏBƏQƏSİNİN ƏMƏLƏGƏLMƏSİNİN TƏDQİQİ

**T.N. Ağayev, F.N. Nurməmmədova**

***Xülasə:*** Radiasiya-termiki işlənməyə məruz qalmış metallik berilliumun su il təmasında gedən termiki və radiasiya-termiki proseslərdə molekulyar hidrogenin əmələgəlmə kinetikası T=573÷673K temperatur intervalında tədqiq olunub. Molekulyar hidrogenin əmələgəlmə sürətləri və radiasiya kimyəvi çıxımları $G(H_2)$ hesablanmışdır. Müəyyən olunmuşdur ki, tədqiq olunan temperatur intervalında (T=573÷673K) molekulyar hidrogenin radiasiya-kimyəvi çıxımı $G(H_2)$ 13,6-dan 22,1 molekul/100eV-a qədər artır. T=673K temperaturda radiasiya-termik işlənmiş berilliumda oksid təbəqəsinin səthinin nisbi dəyişmələri, elektrik hərəkət qüvvəsinin (e.h.q.) qiymətləri hesablanmış və şüalanma müddətindən asılılıq qrafikləri qurulmuşdur.

***Açar sözlər:*** Berillium, qamma şüaları, oksid təbəqəsi, hidrogenin toplanması, elektrik hərəkət qüvvəsi