Protective Coating of Irradiation Device for Fast-Neutron Reactor

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Abstract. The objective of this paper is to select a coating on the surface of zirconium hydride (ZH) in order to reduce hydrogen losses under the operating conditions of an irradiation device of FN-reactors. Tests were carried out on the samples of the moderator units made of zirconium hydride. Oxide, phosphide-oxide and oxide-enamel coatings were considered as a protective layer. Hydrogen yield out of the ZH was studied using a calorimeter and a mass spectrometer by thermal heating of the samples according to the test program (heating rate of 10 °C/min, maximum temperature of 1000 °C, isothermal exposure of 40 min, cooling with a furnace). The hydrogen content in the samples was determined by high temperature vacuum extraction. It is shown the oxide coating is the most technologically advanced and effective. A thermogravimetric analysis of the ZH sample with the protective oxide coating was carried out, and the temperature-time dependence of a stoichiometric coefficient (H / Zr) was determined. The amount of the hydrogen released was determined in a temperature range of 20–1100 °C. The temperature increase in up to 1100 °C leads to almost total loss of hydrogen (98–99 %). In this case, the sample retained its integrity, and the coating exfoliated and fragmented.

1. Introduction

At the present time a great demand is observed for the gamma sources based on cobalt-60 isotope (60Co) with a specific activity above 200 Ci/g. Cobalt-60 of a high specific activity is actively used in medicine, for example, in “gamma-knife” installations used in the field of cancer therapy [1].

A nuclear reactor with a high flux density is required for the isotope production; such feature is typical for fast sodium reactors. At the same time the low cross-sections of nuclear reactions in the “fast” neutron spectrum do not allow producing an acceptable specific activity. An irradiating device with a moderator made of zirconium hydride (ZH) allows combining the advantages of the intense neutron flux, which is typical for fast reactors, and the thermal neutron spectrum typical for thermal reactors [2].

Zirconium hydride ZrH1.85 is considered as a moderator. The moderator is required to increase a neutron capture rate in the material to be produced by the neutron spectrum degradation. However, use of zirconium hydride is accompanied with some difficulties, such as low corrosion resistance in the oxidizing medium and large losses of hydrogen at high temperatures [3]. According to the data of [4], at a temperature of 600–700 °C hydrogen is completely released out of zirconium hydride. To eliminate this drawback, protective coatings are applied to the hydride moderator surface. Oxide coatings are considered as the most effective [4].

The objective of this paper is to select a coating on ZH surface in order to reduce the hydrogen loss under the operating conditions of the irradiation device.
2. Test procedure

It has been the experience of the moderator operation based on zirconium hydride as a structural element of the reactor core that the following types of barrier layers have the required hydrogen-restraining properties: oxide, oxide-phosphide, and oxide-phosphate-enamel coatings. In the framework of this paper the following coating formation methods have been considered:

- electrochemical deposition of the oxide coating in the solution of chromium anhydride;
- temperature phosphidation of the sample surface;
- formation of the oxide coating by anodizing of the sample surface;
- low-temperature enameling of the sample surface samples;
- formation of the oxide coating by thermal heating of the sample in an oxygen-containing medium;
- a superposition of the above mentioned methods.

Electrochemical deposition of the oxide coating in the solution of chromium anhydride was carried out using a galvanization plant. To form an anode film the samples of zirconium hydride were placed in the bath, which serve as positively charged electrodes during its anodization. A constant voltage was applied between the electrodes and an electric current was passed for 15–20 min.

Phosphide-oxide coating was applied in accordance with the following operations:

1) phosphidation of zirconium hydride. The samples were placed in a boat and filled with phosphorus then the boat with the samples was located inside a horizontal flow furnace and heated to a temperature of 300–350 °C in an argon flow. The exposure time is up to 3 hours;

2) anodic oxidation of the samples. The process was carried out in the bath for electrolysis in the solution of nickel sulfamate at the room temperature.

The oxide-enamel coating was formed as follows:

1) preparation of a solution for coating;
   - preparation of dry frit by mixing the starting components;
   - heat treatment of the frit, grinding and manufacturing an enamel solution;
2) formation of the oxide coating by an electrochemical method in the solution of chromium anhydride;
3) applying of a thin layer of the prepared solution to the sample surface and drying for 2–3 hours at the room temperature;
4) heat treatment of the samples at 800–850 °C for 2 min.

The samples analysis consisted of a visual inspection using a stereographic microscope, measurement of geometric and weight parameters and study of the thin sections of longitudinal and cross sections with the use of electron and optical microscopy. Coating continuity was assessed by a capillary inspection.

The hydrogen yield out of zirconium hydride was studied using Netzsch DSC 404F1 calorimeter and Netzsch QMS 403 mass spectrometer. The test object is cylindrical samples made of zirconium hydride with a diameter of 5.0 ± 0.5 mm and a height of 3.0 ± 1.0 mm.

The test procedure was as follows: a zirconium hydride sample was placed in the ceramic crucible located in the high-temperature calorimeter furnace. After that, the system was flushed with an inert gas to remove the impurity compounds adsorbed on the chamber surface. Next, the sample was heated thermally according to the test program. A signal was recorded from the mass spectrometer in the form of ion currents distribution by atomic mass units. Based on these currents magnitude a conclusion was made on the gases presence in the mass spectrometric chamber. By changing the ion current, one can judge the beginning of the gas yield out of the sample, as well as this gas composition.

Thermogravimetric analysis (TGA) was performed to quantify the yield of hydrogen out of the zirconium hydride samples. The measurements were performed on Netzsch STA 409 CD synchronous thermal analyzer with Aeolos QMS quadrupole mass spectrometer in the high-temperature furnace with a graphite heater and a protective ceramic tube. The sample was placed in the crucible made of beryllium oxide and then put it on the TG holder of the sample on two Al₂O₃ separation discs. Heating was carried out according to the following temperature program:

- preheating up to 50 °C at a rate of 5 °C/min, isothermal exposure was 5 min;
- heating up to 515 °C at a rate of 5 °C/min, isothermal exposure was 1 h;
- heating from 515 to 1100 °C at a rate of 20 °C/min;
- cooling to 220 °C at a rate of 20 °C/min.

3. Test results

3.1. Oxide coating

Figure 1 shows the exterior view of the zirconium hydride sample with the oxide coating. The oxidation results in formation of the anodic oxide layer with a thickness of 5–15 μm on zirconium hydride. The coating on the sample is black and shiny, without any signs of exfoliation and flaking off. A capillary control of the sample surface did not detect the presence of discontinuities, pores, or cracks in the coating. The results of metallographic analysis of the sample are shown in Figure 2.

![Figure 1](image1.png)

**Figure 1.** Exterior view of ZH sample with oxide coating.

![Figure 2](image2.png)

**Figure 2.** Metallographic analysis of ZH sample with oxide coating.

Additionally, a fractographic analysis of the sample was carried out in order to assess the oxide coating adhesion to the surface of zirconium hydride. Figure 3 presents a photo of the fracture surface of the sample obtained using a scanning electron microscope.

A mechanism of zirconium hydride destruction is a fragile cleavage. The micro relief of the fracture surface is relatively developed. The cleavage planes have different directivity due to the corresponding orientations of individual grains. The cleavage steps available in the form of a knobby fracture inside individual grains are noted. It indirectly indicates the purity of the grain boundaries of zirconium hydride.

Facets of the oxide coating fracture surface are also identified as a cleavage. However, the micro relief of the coating cleavage is less developed, which is due to the smaller grain size in comparison with zirconium hydride. No traces of the coating exfoliation are available.

![Figure 3](image3.png)

**Figure 3.** Fractographic analysis of zirconium hydride sample with oxide coating.

Qualitative thermal tests of this sample with the use of a calorimeter and mass spectrometer showed the absence of hydrogen yield up to a temperature of 600 °C. It should be noted the beginning of the
samples dehydrogenation without a protective coating is observed at a temperature of 500 °C [5]. Based on the results obtained, it can be concluded that the thermogravimetric analysis is advisable. The results are shown in Figure 4.

![Figure 4](image-url)

**Figure 4.** TG –curve of zirconium hydride sample with oxide coating.

According to the analysis results, it was noted that at an isothermal exposure of 515 °C and up to 700 °C the hydrogen yield and change in the sample mass were not observed. The temperature of the hydrogen yield beginning is 700–720 °C. The mass fraction of hydrogen released at 900 °C is ~ 0.2 %. An increase in temperature from 900 to 1100 °C leads to the total loss of hydrogen (98–99 mass %). The specific change in the sample weight as a result of the test was 2.0 % that corresponds to the total yield of hydrogen out of the sample. It should be noted that the sample retained its integrity, and the coating exfoliated and fragmented.

### 3.2. Phosphide-oxide coating

The exterior view and electron microscopic image of the sample after applying the phosphide-oxide coating are shown in Figures 5 and 6. It should be noted the coating was formed on the entire surface of the sample; no fracture and exfoliation were observed. The coating is uniform; its thickness varies from 5 to 8 microns. Metallographic analysis showed that “bare” sections of zirconium hydride were not detected. However, some defects within the coating were detected. The defects can be caused both by technology and sample preparation during grinding.

![Figure 5](image-url)

**Figure 5.** Exterior view of zirconium hydride sample with phosphide-oxide coating.

![Figure 6](image-url)

**Figure 6.** Metallographic analysis of zirconium hydride sample with phosphide-oxide coating.
According to the thermal tests results the beginning of dehydrogenation of the sample with a phosphide-oxide coating is observed at a temperature of ~ 540 °C, that is slightly higher than the “average” hydrogen yield temperature of ~ 500 °C. Thus, the hydrogen-restraining effect of the protective coating obtained by this method is not significant.

In addition, the samples phosphidation stage is technologically complicated, and it is accompanied with formation of a toxic substance - white phosphorus.

3.3 Oxide-enamel coating

Fig. 7 shows an electron microscopic image of the surface of the zirconium hydride sample coated with an oxide-enamel coating. As it can be seen from Figure 8, the thickness of the oxide layer is ~ 3 μm, and the enamel coating thickness varies from 10 to 20 μm. The coating is smooth and shiny, and numerous bright inclusions have been detected.

The performed thermal tests showed the temperature at which hydrogen began yielding out of the sample was ~ 500 °C, that is, the enamel layer available both did not increase the dehydrogenation temperature, and it also negatively affected the stoichiometric stability of the oxide-coated sample. The post-test analysis showed that numerous cracks appeared on the sample surface which apparently caused the loss of the protective properties of the coating (Figure 9).

In addition to the hydrogen-restraining properties loss during the thermal tests, it should be noted that a technological process of the enamel application includes the heat treatment at a temperature above 800 °C for 2 minutes. Despite the fact this process is carried out rather quickly, some quantity of hydrogen can yield out of the product. Thus, at this stage of development, it is impossible to recommend the oxide-enamel coating for use as a protective layer for the zirconium hydride moderator.
4. Conclusion

The paper presents the results of a study of samples of moderator units made of zirconium hydride with protective coatings. Oxide, phosphide-oxide and oxide-enamel coatings were considered as a protective layer. Hydrogen yield out of the ZH was studied using a calorimeter and a mass spectrometer by thermal heating of the samples.

According to the tests performed, we can conclude that the most effective and technological is electrochemical application of the oxide coating in the chromium anhydride solution, that prevents the hydrogen yield up to temperatures of 700 °C. The temperature increase in up to 1100 °C leads to almost total loss of hydrogen (98–99 %).

References

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