Fabrication processes and testing of the moderator for irradiating devices of BN reactors. Testing of the moderator

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Abstract. The work presents the results of studies of zirconium hydride used as the moderator for irradiating devices in fast reactors. Zirconium hydride fabrication process using methods of direct saturation of the source material and powder preparation and compacting has been optimized. Hydrostatic method was used to measure density of the samples; for the samples produced by direct saturation density varies within 5.61 to 5.65 g/cm³, for compacted zirconium hydride - 5.45 to 5.55 g/cm³. Tests to evaluate hydrogen release from zirconium hydride have been conducted. It has been shown that dehydration onset temperature is (420 – 450) °C (powder compaction method) and (500 – 550) °C (direct saturation method). It has been noted that in 20 minutes of the sample heating from 500 to 900 °C, the mass fraction of the hydrogen released is 0.6 %. The results acquired confirm the data on diminished thermal stability of zirconium hydride produced by the powder method in gaseous media.

1. Introduction

Metal hydrides found a wide application in a number of industries as hydrogen sources, reducing agents for production of ultra-pure metals, catalysts, etc. The interest in hydrides in nuclear industry stems from the opportunity to use them as the materials for moderators, reflectors and protective shielding, especially for high-temperature propulsion nuclear reactors [1].

Use of a hydride-based moderator makes possible a significant reduction of the critical mass of the fissile material thereby reducing the dimensions and weight of the reactor itself. To this end, developers of the nuclear power units (NPU) pay close attention to hydrides as prospective moderator materials.

Of all hydrides, zirconium hydride of ZrH₁₈₅ is the one most widely used in Russia. Since 1980s it has been employed as “trap-rods” of BOR-60 reactor, with control and protection system rods of similar design being successfully used in BN-350 and BN-600 reactors. Special irradiating devices containing zirconium hydride used for production of gamma-emitters based on ⁶⁰Co had been developed and are employed in the lateral blanket of the BN-600 reactor [2]. Moderator blocks made of zirconium hydride were used in TOPAZ-1 nuclear power units as components of space vehicles [3]. The HTRE-3 nuclear reactor had been developed in the US to serve as an aircraft propulsion unit [4]. Zirconium hydride was used as the moderator with no hydrogen losses during operation for 100 hours at a temperature of 700 °C. These and other cases confirm the high efficiency and operational capabilities of the products made of zirconium hydride under conditions typical for nuclear reactor cores of various types, especially those operating on fast neutrons.
Zirconium hydride workpieces are usually made by through (direct) saturation of metallic workpieces or by formation of briquettes made of metal hydride powders with their subsequent compacting.

Through saturation or through hydrogenation means diffusive saturation of the metal workpiece to obtain certain hydrogen content in its bulk. An important advantage of the method of small workpieces hydrogenation is the capability to produce the pore-free material and relatively simple production chart. The drawbacks of this method are the considerable time consumption of the workpiece saturation with hydrogen, with processing of a large workpiece requiring up to several weeks and the necessity to employ autoclave equipment in the most cases.

Employment of the method of products formation from metal hydride powders ensures a high production output of the source hydride powders and provides the capability to produce composite materials. The main drawback of the material produced from powders is imperfection of intergranular boundaries resulting in poor resistance to corrosion in gaseous media.

2. Experimental

Production of compact zirconium hydride workpieces was carried out using the “UPS-1” direct synthesis apparatus specially designed for LUCH FSUE [5]. In general, the process of zirconium hydrogenation involves metered supply of hydrogen at a temperature of (600 – 800) °C depending on the required extent of saturation of the material. As the pressure in the ampoule rose to the atmospheric the samples were cooled down to the room temperature in the furnace.

It is worth noting that as the zirconium workpieces get saturated with hydrogen their volume increases noticeably (density of zirconium is 6.5 g/cm³, density of zirconium hydride in ε-phase is 5.6 g/cm³). To reduce the scope of the laborious machining of hydride workpieces their dimensions are to be chosen with minimal machining tolerances.

Zirconium hydride workpieces produced by direct saturation were used as the feedstock when the powder compacting method was employed. The workpieces were ground down to a particle size of less than 400 μm using an impact-jet mill. The particle sizes of the powders were monitored using an Analysette 22 laser analyzer of particle size. Subsequently, the method of powder workpieces deformation in steel casings was employed to produce compact products.

Hydrogen content in the samples was measured by high-temperature vacuum extraction using a LECO RH-402 analyzer. The principle of operation of the analyzer is based on high-temperature hydrogen extraction in inert gas flow in a reducing or neutral medium in an induction furnace with temperature programming up to 2800 °C. The extracted hydrogen is then removed by the carrier gas (nitrogen) through the purging system for removal of impurities and transported into a high-sensitivity heat conductivity sensor.

The zirconium hydride samples were weighed using high-precision electronic scales made by VIBRA. Experimental density was measured by hydrostatic method in automatic measurement mode. Besides experimental density, the density of the ideal pore-free material (“theoretical density”) was measured, which was calculated according to reference data and X-ray phase analysis results using the following equation:

\[ \rho_i = \frac{A \cdot z}{N_a} \cdot \frac{1}{V}, \]

where \( A \) is the atomic mass of all the elements in the compound, a.m.u.; \( z \) is the number of formula units per unit cell; \( N_a \) is the Avogadro constant, mol\(^{-1}\); \( V \) is the unit cell volume, Å\(^3\).

Zirconium hydride samples were studied using a D8 ADVANCE X-ray diffractometer. CuK\(\alpha\) X-rays were used. The smoothest surfaces with suitably large areas were chosen to serve as reflective faces.

Quantitative assessment of porosity of the material was performed using the Vestra Imaging System code for image analysis, using automatic functions of calculation of the volume fraction of the area of the objects (per area unit, %) and report preparation.
Studies of hydrogen release from zirconium hydride were conducted using a Netzsch DSC 404F1 calorimeter and a Netzsch QMS 403 mass-spectrometer. The testing procedure was as follows: the zirconium hydride sample was placed into a ceramic crucible made of Al₂O₃, placed into the high-temperature furnace of the calorimeter. Then the system was flushed with inert gas to remove impurities adsorbed at the surface of the chamber. Then the sample was heated according to the test procedure (heating rate 10 °C/min, maximum testing temperature 1000 °C, isothermal exposure 40 min., cooling simultaneously with the furnace).

Thermogravimetric analysis (TGA) has been performed to make qualitative assessment of hydrogen release from the samples. The measurements were carried out using a Netzsch STA 409 CD synchronized thermoanalyzer with a QMS Aeolos quadruple mass-spectrometer in a high-temperature furnace with a graphite heating element and a protective ceramic tube. The sample was placed into a ceramic crucible made of beryllium oxide and mounted on a TG sample holder on two separating discs made of Al₂O₃. Heating was conducted according to the following scenario:

1) Preheating up to 50 °C at a rate of 5 °C/min, isothermal exposure 5 min;
2) Heating up to 1200 °C at a rate of 20 °C/min;
3) Cooling down to 220 °C at a rate of 20 °C/min.

3. Results and discussion

In accordance with the process operations described above, zirconium hydride samples were fabricated using the direct saturation method and powder production and compacting process. The X-ray diffraction patterns were indicated as belonging to body-centered tetragonal structure (I4/mmm spatial group), corresponding to zirconium hydride ε-phase (the closest to ZrH₂).

Structure of the samples in the cross-section is shown on figure 1. For niobium-doped zirconium hydride, banded substructure of hydride ε-phase is typical. Banding is not very distinctive. The boundaries of the original metallic alloys are clearly visible, because the impurities are precipitated at the grain boundaries. Microstructure of the samples produced by compaction of powders is marked by presence of “small” (up to 30 μm) pores and the extent of porosity varies between 1 and 1.5 %.

![Figure 1](image.png)

**Figure 1.** Structure of samples of zirconium hydride produced by direct saturation of material (a) and by powder compaction (b).

According to the results of hydrostatic weighing, the density of the samples produced by direct saturation is (5.61 – 5.65) g/cm³, and that of compacted zirconium hydride samples is (5.45 – 5.55) g/cm³, which makes up (98 – 99) % of the theoretical density.

Studies of hydrogen release from zirconium hydride samples fabricated using direct saturation method were conducted in accordance with the procedure described in Section 2. Maximum test temperature was 700 °C, exposure – 40 minutes. This experiment made possible to define the hydration onset temperature which is equal to (500 – 550) °C.
The same tests were conducted for the samples of zirconium hydride produced using the powder compaction process. Here, the maximum test temperature was reduced to 550 °C. Hydrogen release onset temperature was found to be (420 – 450) °C.

To make a qualitative assessment of hydrogen release from zirconium hydride samples, thermogravimetric analysis (TGA) has been conducted. A compact zirconium hydride sample \((\text{C}(\text{H}) = (2.02 – 2.08) \%)\), produced by powder compaction method, was placed into the center of a crucible and heated up according to the temperature scenario described in Section 2 to the maximum temperature equal to 1200 °C. Onset of the mass loss was observed at a temperature of 495 °C (figure 2). Four stages of the mass loss are clearly discernible on the TG-diagram; on the MS-diagram the two first peaks converged and are hard to distinguish. However, it can be said with surety that the mass loss is caused by hydrogen release.

**Figure 2.** Thermogravimetric (TG) and Mass-spectrometric (MS) diagrams of zirconium hydride decomposition (powder method).

Presence of several peaks on the mass-spectrometric diagram of hydrogen can be due to:
- Occurrence of hydrogen release from the samples in stages when at a given temperature the minimum allowable residual hydrogen concentration in the sample is gained and further hydrogen release may occur only with further elevation of temperature;
- Change of diffusion rate and velocity of hydrogen atom migration towards the surface of zirconium hydride.

Analysis of figure 2 allows to make a quantitative assessment of hydrogen release from the zirconium hydride sample. Throughout the period of (20 – 25) min during sample heating from 500 to 900 °C the weight fraction of the escaped hydrogen reached ~ 0.6 %. As the temperature reached 1100 °C the weight fraction of the hydrogen released from the sample is equal to 1.0 %.

Having analyzed the mass-spectrometric diagrams of zirconium hydride decomposition by oxygen (32), water (18), hydroxide ion (17) and hydrogen (2) the following conclusions can be made:
- Hydrogen release onset temperature (according to the hydrogen diagram) is (495 – 500) °C (the same conclusion was made from the TG-diagram analysis);
- Deviation of the registered parameters from the background value for water and hydroxide ion (OH) was observed somewhat earlier, at a temperature of (420 – 430) °C.

Thus, the hydrogen release onset temperature for the zirconium hydride sample made by powder compaction has been confirmed to be (420 – 430) °C.

The results acquired confirm the assertion that thermal stability of zirconium hydride produced by the powder method is diminished in gaseous media.

**4. Conclusion**

Zirconium hydride samples have been fabricated by both direct saturation of the original metal and powder production and compaction. Basing on the materials science studies, the characteristics of the samples have been determined (Table 1).
Table 1. Results of materials science studies of zirconium hydride samples.

| Method                  | Hydrogen weight fraction (\%) | Phase composition | Density (g/cm³) | Porosity (%) |
|-------------------------|-------------------------------|-------------------|-----------------|--------------|
| Direct saturation       | 2.02 ± 0.05                  | ε-phase ZrHₓ      | 5.61 – 5.65     | –            |
| Powder compaction       | 2.07 ± 0.05                  | ε-phase ZrHₓ      | 5.45 – 5.55     | 1.0 – 1.5    |

It has been demonstrated that the method of thermogravimetric analysis of zirconium hydride experimental samples is applicable for quantitative substantiation of behavior of zirconium hydride moderator at operational temperatures ~ 510 °C, as well as during extraction from the core (900 – 1100 °C). The analysis of thermal tests allowed to establish the temperature-time dependencies of hydrogen release up to 1100 °C. It has been shown that ZrH₂ dehydrogenation temperature is (420 – 450) °C (powder compaction method) and (500 – 550) °C (direct saturation method). It was noted that throughout the period of (20 – 25) min during sample heating from 500 to 900 °C the weight fraction of the escaped hydrogen reached ~ 0.6 %. As the temperature reached 1100 °C the weight fraction of the hydrogen released from the sample is equal to 1.0 %.

References

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