

---

NEW METHODS OF TREATMENT AND PRODUCTION  
OF MATERIALS WITH REQUIRED PROPERTIES

---

## Peculiarities of Application of the Gas Extraction Method for Determination of Hydrogen Content in Samples of Irradiated Zirconium Materials

G. V. Shishalova<sup>a, \*</sup>, G. P. Koblyansky<sup>a, \*\*</sup>, A. A. Sheldyakov<sup>a, \*\*\*</sup>,  
V. Yu. Shishin<sup>a, \*\*\*\*</sup>, and A. M. Novikov<sup>a, \*\*\*\*\*</sup>

<sup>a</sup>State Scientific Center Research Institute of Atomic Reactors—NIIAR,  
Dimitrovgrad, Ulyanovsk oblast, 433510 Russia

\*e-mail: orm@niiar.ru

\*\*e-mail: gpk@niiar.ru

\*\*\*e-mail: aasheldyakov@niiar.ru

\*\*\*\*e-mail: Shishin@niiar.ru

\*\*\*\*\*e-mail: orm@niiar.ru

Received June 5, 2018; revised August 10, 2018; accepted August 10, 2018

**Abstract**—Results of multiyear research of zirconium materials from nuclear reactors show that the hydrogen content measured by a high-temperature extraction method does not always correlate with the number and size of zirconium hydrides measured by metallography. Additional examinations found that hydrogen is contained not only in the metal but also in the oxide film of samples under examination. This means that the level of hydrogenation of zirconium materials under irradiation should be estimated by the hydrogen content in metal only to allow for a correct comparison of the results of gas analysis and metallographic investigations. In this connection, the hydrogen content was measured separately in the metal and in the oxide film. A device to mechanically remove sediments and oxide film from samples was developed. However, when removing the oxide mechanically, a top layer of metal is also removed, as a rule, which leads to an uncontrolled increase in the measurement error because of a nonuniform distribution of hydrides in the metal. The assessment of the contribution of oxide hydrogen using a curve “total hydrogen content vs. oxide film thickness” showed no distinct dependence. Moreover, it was stated that the results of the total hydrogen content measurements by the high-temperature extraction method can be affected by the elementary composition of sediments and oxide films on the surfaces of spent items. The performed research resulted in the development of a technique to measure the hydrogen mass fraction by high-temperature extraction in an inert gas flow separately in the metal and oxide film without any preliminary mechanical removal of the oxide. This will allow examining the dependence between the hydrogen content in the oxide film and its thickness, as well as estimating a possible correlation between the hydrogen mass fraction in the metal and the quantitative characteristics of hydrides measured by a metallographic image.

**Keywords:** zirconium alloys, gas extraction method, hydrogen content measurement, oxide films

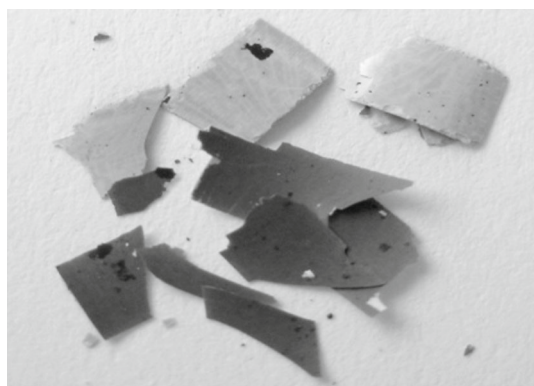
**DOI:** 10.1134/S2075113319030390

### INTRODUCTION

The main construction material for critical elements of heat-releasing assemblies of water-cooled power reactors are zirconium alloys, which are prone to absorption of hydrogen. It is well known that hydrogen plays an important role in formation and development of defects in zirconium products during their operation in a reactor. Depending on the level of hydrogen content and operating temperature, hydrogen may be present in the metal as a solid solution or as hydrides. Hydrides have a significant embrittlement effect, since they can serve as regions of crack formation and development. Therefore, it is important to

know the critical concentration of hydrogen at which formation of hydride release starts in zirconium alloys. Study of the mechanisms of processes occurring at the same time depending on the operating conditions is an indispensable component of postirradiation investigations using sensitive and accurate methods of quantitative analysis of hydrogen content.

For about 30 years, the hydrogen content in irradiated samples at NIIAR was determined using the method of spectral isotope balancing [1]. Selection of the gas probe for research was performed in a vacuum unit located in glove box, and gas was analyzed on a spectral analysis device. The method does not require



**Fig. 1.** Two-layer oxide film chemically removed from the metal of the ring sample cut off from cladding of a fuel rod.

using references and complete extraction of gas from a sample; however its disadvantages include long duration and large labor intensity of analysis as well as technical difficulties connected with repair of the unit. Introduction of computer recording and software made it possible to reduce the time of processing the results and decrease measurement errors; however, the total analysis duration did not change (one sample per shift).

Significant growth of materials science research led to the necessity of using a new express analysis method. In this connection, the method of high-temperature extraction in a stream of inert gas (HTEIG) [2] was introduced in 2002 on the basis of an ELTRA OH 900 gas analyzer and the corresponding methodology was developed [3].

Comparison of analytical characteristics of the extraction method with the spectral isotope balancing method performed using standard samples and zirconium hydride showed the advantage of the extraction method, which allows analyzing up to 20 samples per shift with almost 3.5 times less relative measurement error.

Analysis of postirradiation examinations showed that the degree of hydrogenation of irradiated zirconium materials determined by the HTEIG method does not always correlate with the amount and sizes of hydrides registered on metallographic shots [3]; at the same time, no regularity in discrepancy of results was detected.

Apparently, one of the main reasons for discrepancy in the results obtained by different methods is the fact that in metallographic investigations hydride inclusions are studied only in the metal of a sample without accounting for its oxide film, while the HTEIG method is used to measure the total content of hydrogen in a sample. In addition, the results of metallographic analysis may be influenced by the etching regime, cooling rate of the product after operation, and also different orientation of zirconium hydrides [4, 5].

Investigations of the chemical content of irradiated zirconium samples confirmed that a layer of sediment of varying thickness and quantitative elemental composition is usually formed on the surface of oxide film [6]; at the same time, hydrogen is contained not only in the metal but also in the oxide film.

Analysis of reference data and our own results obtained earlier shows that the hydrogen content in irradiated samples measured by the HTEIG method may influence each of these factors. The aim of this work is a deeper study and accounting for factors influencing measurement results of hydrogen content in irradiated samples of zirconium materials.

## EXPERIMENTAL

Standard ELTRA OH 900 gas analyzers are not intended for investigating irradiated materials; thus, this model was created according to a special order with a remote furnace block, which allowed producing a gas analyzer unit for performing postirradiation examinations by reconstruction of the safety glove box and positioning the furnace block in it.

The method of analysis is based on high-temperature melting of sample in a graphite pot in flux of an inert gas, extraction of gases contained in sample, cleaning of gases from carbon oxides, and further quantitative measurement of extracted hydrogen using a thermal conductivity detector and oxygen using an infrared cell.

All the planned investigations were split into several stages. At the first stage, the possibility of chemical separation of oxide film from metal was studied, since the main problem was to determine the content of hydrogen only in the metal of the irradiated sample. At the second stage, mechanical removal of the oxide film was accomplished by a special device located in the safety glove box. The third stage of investigation was devoted to studying the possibility of accounting for the contribution of hydrogen contained in the oxide film to the total content of hydrogen in the sample depending on the thickness of this film.

## RESULTS AND DISCUSSION

It is well known that metallic zirconium and its oxide dissolve in different chemical media; however, all conducted experiments led to the fact that the metal was dissolved first and the oxide film was maintained, and then it could be dissolved in another medium. It is necessary to note that an oxide film thicker than 25–30  $\mu\text{m}$  in most cases turned out to be double layered, but in some cases, it could also have three layers, two of which were detached from each other during dissolution (Fig. 1).

Analysis of oxide film obtained in this way by the HTEIG method is not only technically complicated but is also an incorrect problem because of a very small

mass of oxide (~4–20 mg). Nevertheless, some of such measurements were performed and confirmed the presence of hydrogen in oxide film of irradiated samples. In this case, the content of hydrogen in the metal was determined by subtraction of the mass fraction of hydrogen in oxide from the total content of hydrogen in a similar but different sample, which was studied together with oxide film. Hydrogen was also discovered in oxide films of unirradiated samples after primary oxidation [3].

Postirradiation studies of various zirconium materials showed that sometimes it can be seen visually on the surface of irradiated samples (Fig. 2) that the metal should be cleaned from the oxide layer or the contribution of oxides to the total content of hydrogen in the sample should somehow be taken into account. The mass fraction of hydrogen in samples shown in Figs. 2a–2c was 0.0076, 0.0190 and 0.0272%, respectively.

At the second stage, ring-shaped and flat samples (Fig. 3) before and after mechanical removal of oxide films from outer and inner sides were studied. The sizes of ring-shaped samples (diameter of ~6–13 mm) and fragments of products made of zirconium alloys were specified by optimal mass for analysis (100–250 mg). Table 1 presents the results of investigation for three different samples, where the content of hydrogen in oxide film was determined by subtraction of the mass fraction of hydrogen measured in metal (sample with removed oxide film) from the total amount of hydrogen in the initial blank sample (with oxide film). It can be seen that content of hydrogen varied for different samples not only in the metal but also in the oxide film.

We note that it is not easy to visually estimate completeness of oxide film removal in the safety box during mechanical removal, and in this case, not only the oxide layer but also the base metal itself may be removed; in some cases, the operation of surface cleaning must be repeated, but on another similar sample. Table 2 shows data on the hydrogen content in samples of zirconium alloy E635 at different stages of oxide film removal from the surface.

In this way, it appears that, in order to measure the content of hydrogen in metal correctly, it is necessary to analyze a bunch of samples from one and the same region of irradiated material. At the same time, it is known that even samples cut off from neighboring regions of the same product are not absolutely identical from the point of view of hydrogen content in them. In addition mechanical removal of the oxide layer partially removes the upper layer of metal, which leads to uncontrollable growth of measurement errors taking the nonuniformity of distribution of hydrides in metal into account. Finally, high labor intensity of mechanical removal of oxides leads to an increase in radiation doses to personnel during operation with irradiated samples.

The third stage of investigations on studying the influence of the thickness of oxide film on its contri-

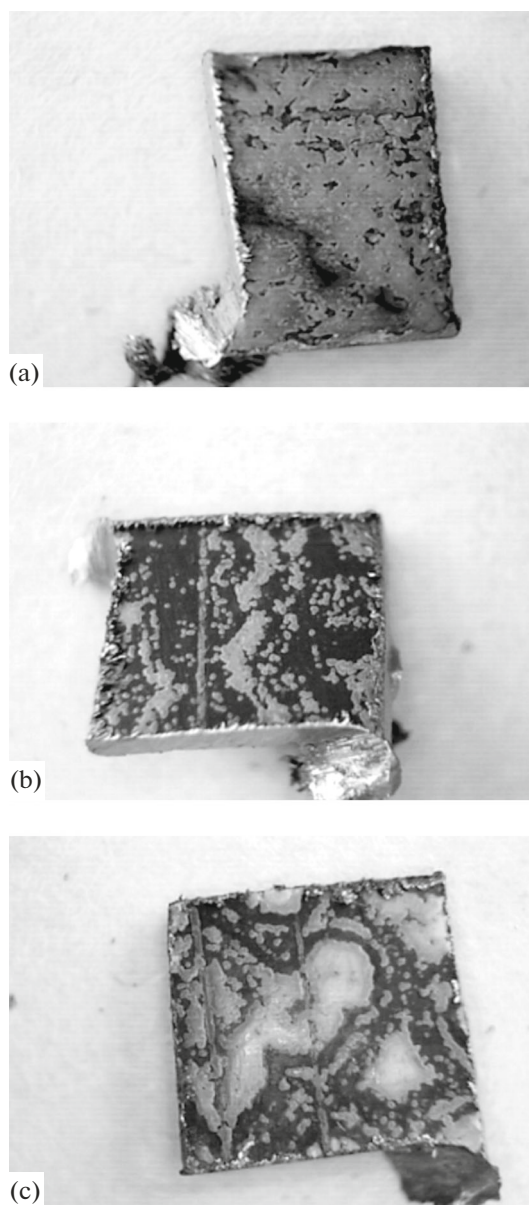


Fig. 2. Irradiated samples contain 0.0076 (a), 0.0190 (b), and 0.0272 wt % (c) before oxide film removal.

bution to the total hydrogen content in sample, which was undertaken in this connection, did not lead to satisfactory results either; this is confirmed by our and reference data [3, 8–10]. Additionally, it was established that the total content of hydrogen measured by the HTEIG method does not coincide with data of metallographic analysis on determining the amount and sizes of hydrides existing in them. Values obtained by the HTEIG method can be not only larger (which seems natural) but also less than values obtained in metallographic studies.

Such a discrepancy can be explained by considering the properties of oxides themselves. It is well known that hydrogen is able to restore most metals



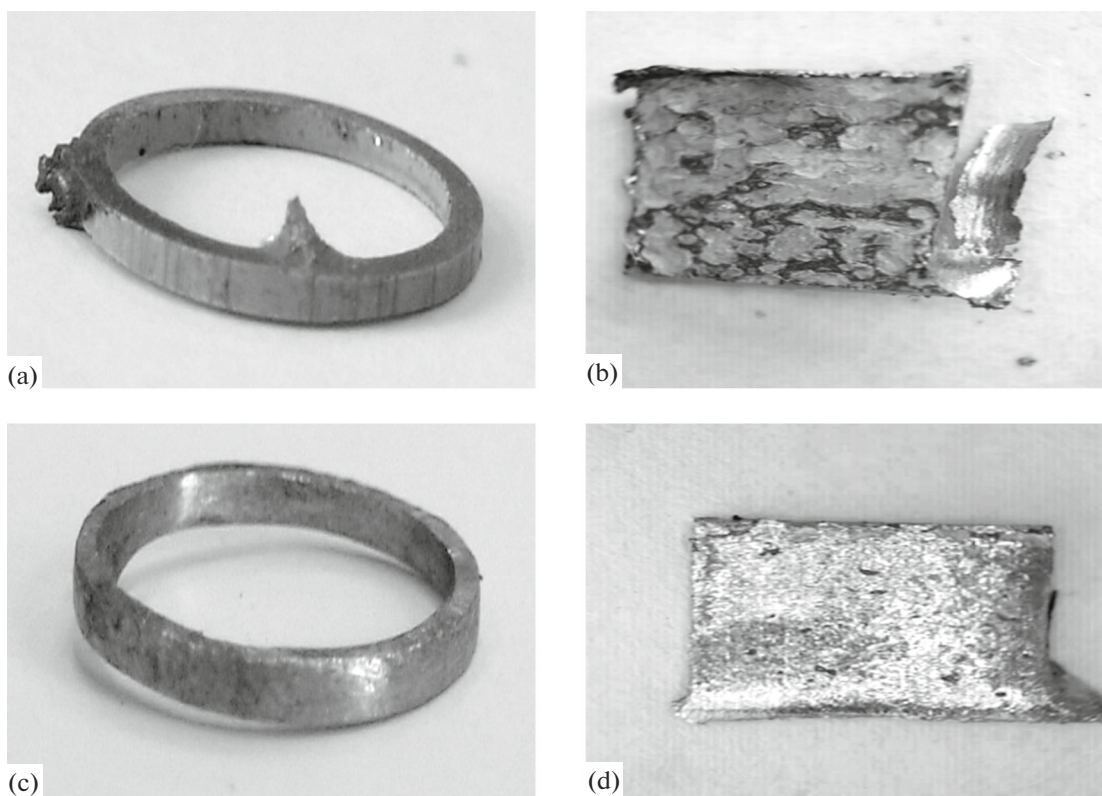


Fig. 3. Ring (a, c) and flat (b, d) samples before (a, c) and after (b, d) mechanical removal of oxide films.

from their oxides with formation of  $H_2O$  by reactions like  $2MeO + H_2 \rightarrow 2Me + H_2O$ .

For example heating of any iron oxide to temperature over  $400^\circ C$  leads to restoration of iron by hydrogen:  $Fe_2O_3 + 3H_2 = 2Fe + 3H_2O$ .

Hydrogen can also be used to restore other metals in the series of standard potentials after manganese: V, Nb, Cr, Zn, Ga, Fe, Cd, In, Tl, Co, Ni, Te, Mo, Sn, Pb, etc. Therefore, the presence of a layer of sediments and oxide film on the surface of sample containing some amount of iron oxides or other elements may affect the results of measurement of hydrogen content. This means that part of hydrogen in the form of  $H_2O$  may be absorbed by the adsorbent located after the infrared cell, which decreases the amount of hydrogen registered by the thermal conductivity cell.

Spectrometric analysis of the elemental composition of sediments and oxide films on the surface of samples of structural zirconium [6] did show the presence of Fe, Cr, Ca, Mg, etc. (Table 3). It is necessary to note that qualitatively the elemental composition of sediments and oxide films on samples without fuel and on samples from cladding of fuel elements basically coincides; differences are observed only in the quantitative content of these elements. It was also established that overheating of the cladding of fuel elements leads to chemical interaction of elements of sediments with oxide film resulting in formation of zirconates.

After all three stages of investigations, it became obvious that it is necessary to determine the content of hydrogen separately in oxide film and in metal of samples without mechanical removal of oxide. Such a conclusion is based on the fact that extraction of

Table 1. Mass fraction of hydrogen in irradiated samples

Characteristic	Number of sample		
	1	2	3
Thickness of oxide film (outer layer/inner layer), $\mu m$	30/27	31/24	30/32
Mass fraction of hydrogen in initial blank sample, %	0.0150	0.0209	0.0329
Mass fraction of hydrogen in metal of sample, %	0.0105	0.0186	0.0245
Mass fraction of hydrogen in oxide film relative to mass of sample, %	0.0045	0.0023	0.0084

**Table 2.** Changes in hydrogen mass fraction in the samples of E635 alloy during the oxide film removal

Characteristic of sample	Fragments of directing channel		
	Initial sample with oxide film	Oxide film is removed partially	Oxide film is removed completely
Mass fraction of hydrogen	0.0190	0.0106	0.0056

**Table 3.** Mass fraction of main elements in oxide films

Element	Mass fraction, %			
	Sample 4 (1)	Sample 5 (2)	Sample 6 (3) (light oxide)	Sample 6 (3) (dark oxide)
Fe	0.60	1.29	0.30	3.07
Cr	0.017	0.012	0.008	0.25
Ni	0.012	0.015	0.007	0.25
Nb	0.63	0.67	0.63	0.53
Mg	0.68	0.20	0.22	2.06
Na	3.93	0.13	0.81	14.28
Ca	1.76	0.81	0.46	5.92
Zr	58.71	70.42	59.89	38.96

(1) Layer of sediments from oxide film is preliminarily removed in solution of inorganic acids; (2) oxide film is analyzed together with sediments; (3) layer of sediments from oxide film is preliminarily removed in solution of organic acids.

hydrogen from oxide film occurs at lower temperatures than from metal.

Such measurements became possible at NIIAR after acquisition of a new model of ELTRA OH-900 gas analyzer in 2013 designed specifically for determination of hydrogen content. This device created by special order is not equipped with an infrared cell and the software allows performing stepwise heating of a sample. The use of a more sensitive thermal conductivity detector made it possible to lower the detection limit and measurement error. The presence of a nitrogen generator producing especially pure nitrogen carrier gas (which replaced argon) promoted increasing the reproducibility of results by means of exclusion of an unstable component connected with the quality of argon. The use of a double pot also improved reproducibility of the results of analysis owing to more uniform heating of sample.

The fourth (final) stage of the work was devoted to study and selection of optimal conditions for gas analysis and development of new methodologies to determine the total content of hydrogen separately in oxide film and in metal.

#### METHODOLOGY OF DETERMINING HYDROGEN CONTENT IN OXIDE FILM AND IN METAL

As a result of research, "Methodology of Measuring the Mass Fraction of Hydrogen by High-Temperature Extraction Using Gas Analyzer ELTRA OH 900" was developed and metrologically attested. The meth-

odology of stepwise heating [7] was developed in order to determine the mass fraction of hydrogen separately in metal and in oxide film.

The process of analysis in this case consists of two stages:

—At the first stage, a sample with mass of 100–200 mg is placed into the loading device of the gas analyzer furnace, from where it moves into the preliminarily degassed graphite pot heated to the temperature necessary for extraction of hydrogen only from oxide film without melting of the sample.

—At the second stage, hydrogen is extracted from the metal of the same sample at higher temperature up to complete melting of the sample in the presence of fusing agent (tin). The hydrogen extracted at both stages of the analysis process is passed to the thermal conductivity detector after cleaning from oxides. The analytic program makes it possible to image the process of hydrogen extraction from oxide film and metal graphically as well to process the measurement results in selected units of mass fraction (% or ppm).

Analysis of a large amount of obtained data confirmed the validity of the proposed algorithm of stepwise heating and reliability of results. Table 4 shows the results of analysis for three different samples.

The reliability of results is constantly analyzed and attested by a set of new data obtained on several samples cut off from neighboring regions or on the same sample split into two or four fragments (probes). It was established that the total content of hydrogen measured in one-fourth of the sample (together with oxide

**Table 4.** Hydrogen content in metal of samples nos. 7–9

Number of sample	Mass fraction of hydrogen in metal, %	
	after removal of oxide film by stepwise heating	after removal of oxide film by stepwise heating
7	0.0040	0.0040
8	0.0058	0.0052
9	0.0056	0.0057

**Table 5.** Hydrogen content in irradiated samples nos. 10–12 measured by gradual heating method

Number of sample	Number of probe	Mass fraction of hydrogen in oxide relative to mass of sample, %	Mass fraction of hydrogen in metal relative to mass of sample, %	Total (metal + oxide) mass fraction of hydrogen, %
10	1			0.0137
	2			0.0134
	3	0.0037	0.0098	0.0135
	4	0.0045	0.0099	0.0144
11	1			0.0082
	2			0.0080
	3	0.0021	0.0071	0.0092
	4	0.0025	0.0068	0.0093
12	1			0.0178
	2			0.0177
	3	0.0060	0.0118	0.0178
	4	0.0061	0.0117	0.0178

**Table 6.** Hydrogen content in irradiated samples nos. 13–15 measured by gradual heating method

Number of sample	Mass fraction of hydrogen in metal relative to mass of sample, %	Mass fraction of hydrogen in oxide film relative to mass of sample, %	Total (metal + oxide) mass fraction of hydrogen in sample, %
13	0.0052	0.0160	0.0212
14	0.0057	0.0122	0.0179
15	0.0043	0.0021	0.0064

film) is in agreement with the total content measured separately in metal and in oxide of another fourth of the same sample (Table 5).

Slight discrepancies are possible upon violation of the integrity of oxide film during probe preparation and nonuniformity of hydration along the perimeter of the sample. At the same time, the content of hydrogen measured in the metal of sample does not contradict data of metallographic analysis.

Relevance of the developed methodology is confirmed for example by the fact that it is quite difficult to objectively estimate the correlation of hydrogen in metal and oxide film according to data on the content of hydrogen in samples measured by the standard HTEIG method (metal + oxide) without knowing the exact dependence of hydrogen content on thickness of oxide film. For example, in Tables 6 and 7, it can be

seen that, in different cases, the main contribution to the total content of hydrogen can be made either by oxide film (Table 6) or by metal (Table 7). At the same time, it is necessary to specify that, in the first case (Table 6), the issue is about samples of the same alloy having different thickness of oxide film, while in the second case (Table 7) samples were made of different alloys, but the thickness of oxide film on them was almost identical.

## CONCLUSIONS

(1) It was established that the oxide film on the surface of irradiated products of zirconium alloys contains hydrogen, which makes its own contribution to the total content of hydrogen in sample measured by the HTEIG method. This means that the degree of

**Table 7.** Hydrogen content in irradiated samples measured by gradual heating method

Material of sample	Mass fraction of hydrogen in metal relative to mass of sample, %	Mass fraction of hydrogen in oxide film relative to mass of sample, %	Total (metal + oxide) mass fraction of hydrogen in sample, %
Alloy 1	0.0100	0.0057	0.0157
Alloy 2	0.0083	0.0054	0.0137
Alloy 3	0.0058	0.0061	0.0119

hydration of zirconium materials during the irradiation process should be estimated by the content of hydrogen only in metal; exactly such measurements allow comparing the results of gas and metallographic analysis correctly.

(2) A unit for mechanical removal of the oxide layer from the surface of irradiated samples was designed and created. However, the mechanical method of removing oxides turned out to be quite labor-intensive and in the case of nonuniform distribution of hydrides may lead to increased measurement errors regarding hydrogen content owing to partial removal of the upper layer of metal.

(3) A methodology to determine the mass fraction of hydrogen separately in metal of sample and in oxide film without the necessity of preliminary mechanical removal of the oxide layer was developed.

(4) The developed methodology makes it possible to determine the dependence of hydrogen content directly in oxide film on its thickness as well as to correctly establish the correlation between the mass fraction of hydrogen in metal and quantitative characteristics of hydrides measured by the metallographic method.

### CONFLICT OF INTERESTS

The authors declare that they have no conflict of interest.

### REFERENCES

1. Belokopytov, V.S. and Nazarenko, T.A., Spectral isotope analysis of hydrogen in irradiated materials, *Vopr. At. Nauki Tekh.*, 1975, no. 5, pp. 28–33.
2. Shishalova, G.V., ELTRA OH 900 gas analyzer and its use for determination of hydrogen and oxygen in alloys and hydrides of zirconium, hafnium, and titanium, *X Nauchno-prakticheskii seminar "Analitika–2002," Sankt-Peterburg, 20–22 maya 2002, Tezisy dokladov (X Sci.-Pract. Seminar "Analytics–2002," St. Petersburg, May 20–22, 2002, Abstracts of Papers)*, St. Petersburg: Mezhdunar. Tsentr Ekon., Nauki Tekh., 2002, p. 48.
3. Shishalova, G.V., Zamorskii, D.V., Povstyanko, A.V., and Maerschina, G.I., Determination of hydrogen content in irradiated zirconium alloys, *Fiz. Khim. Obrab. Mater.*, 2009, no. 1, pp. 19–22.
4. Zaimovskii, A.S., Nikulina, A.V., and Reshetnikov, N.G., *Tsirkonievye splavy v yadernoi energetike (Zirconium Alloys in Nuclear Power Engineering)*, Moscow: Energoatomizdat, 1994.
5. Kulakov, G.V., Vatulin, A.V., Kononov, Yu.V., Kosaurov, A.A., Peregud, M.M., Korotchenko, E.A., Shishin, V.Yu., and Shel'dyakov, A.A., The effect of the stress-strain state of irradiated shells of the zirconium-based claddings on the orientation of hydrides, *Vopr. At. Nauki Tekh., Ser.: Materialoved. Nov. Mater.*, 2014, no. 1 (76), pp. 39–48.
6. Shishalova, G.V., Kulakova, M.A., and Povstyanko, A.V., Composition of the deposits on the elements of reactor parts and fuel rod claddings by atomic-emission spectrometry with inductively coupled plasma, *Trudy IX Rossiiskoi konferentsii po Reaktornomu materialovedeniyu, Dimitrovgrad, 14–18 sentyabrya 2009 (Proc. IX Russ. Conf. on Reactor Materials Science, Dimitrovgrad, September 14–18, 2009)*, Dimitrovgrad: Nauchno-Issled. Inst. At. Reaktorov, 2009, no. 3, pp. 52–60.
7. Shishalova, G.V., Shel'dyakov, A.A., Shishin, V.Yu., and Novikov, A.M., Influence of oxide film on determination of hydrogen content in irradiated zirconium alloys by the high-temperature extraction in inert gas flow, *Trudy 5-oi Mezhdunarodnoi konferentsii i 9-oi Mezhdunarodnoi shkoly molodykh uchenykh i spetsialistov im. Kurdyumova "Vzaimodeistvie izotopov vodoroda s konstruktsionnymi materialami," Sarov, 7–11 iyulya 2014 (Proc. 5th Int. Conf. and 9th Kurdyumov Int. School of Young Scientists and Professionals "Interaction of Hydrogen Isotopes with Construction Materials," Sarov, July 7–11, 2014)*, Yukhimchuk, A.A., Ed., Sarov: Ross. Fed. Yad. Tsentr, Vseross. Nauchno-Issled. Inst. Eksp. Fiz., 2015, p. 351–356.
8. Ramasubramanian, N., Perovic, V., and Leger, M., Hydrogen transport in oxide and hydrogen pickup by the metal during out- and in-reactor corrosion of Zr-2.5Nb pressure tube material, *Proc. XII Int. Symp. "Zirconium in the Nuclear Industry," Sabol, G.P. and Moan, G.D., Eds., West Conshohocken, Pa: ASTM Int., 2000, no. ASTM STP 1354, pp. 853–876.*
9. Hermann, A., Wiese, H., Buhner, R., Steinemann, M., and Bart, G., Hydrogen distribution between fuel cladding metal and overlying corrosion layers, *Proc. ANS Int. Topical Meeting on LWR Fuel Performance, April 10–13, 2000, Park City, Utah, USA, La Grange Park: Am. Nucl. Soc., 2000. V. 1, pp. 372–384.*
10. Kammenzind, B.G., Franklin, D.G., Peters, H.R., and Duffin, W.J., Hydrogen pickup and redistribution in alpha-annealed Zircaloy-4, *Proc. 11th Int. Symp. "Zirconium in the Nuclear Industry," Bradley, E.R. and Sabol, G.P., Eds., West Conshohocken, Pa: ASTM Int., 1996, no. ASTM STP 1295, pp. 338–369.*

Translated by K. Gumerov