SECTION 2
PHYSICS AND TECHNOLOGY OF STRUCTURAL MATERIALS

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IMPROVEMENT OF STRUCTURAL MATERIAL FOR FUEL ELEMENT CLADDING OF THE DOMESTIC NUCLEAR REACTORS

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Improvement in the properties, such as corrosion and radiation resistance, of structural zirconium alloys fuel claddings for NPP nuclear reactors by optimizing the Fe content in them is considered. The need to ensure high radiation and corrosion resistance and reliability of fuel claddings for the safe operation of pressurized water reactors of NPPs under operating conditions is substantiated. The technology of magnesium-thermal production of spongy zirconium on laboratory installations has been studied because the using the zirconium sponge as the base of alloys provide safety criteria under LOCA conditions. Experimental studies have shown that the optimization of the Fe content in the Zr-1%Nb alloy leads to an increase in corrosion resistance in the coolant and resistance to radiation growth during irradiation. The processing of the results of the experimental studies made it possible to determine the optimal Fe content for the Zr-1%Nb alloy for fuel claddings.

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INTRODUCTION

Water-cooled thermal neutron nuclear reactors currently dominate the commercial implementation of nuclear energy, and will continue to do so for at least this century. Several countries are building and/or have plans to build many more such reactors in the near future.

The main structural materials for fuel element cladding of water-cooled thermal neutron reactors both in our country and abroad are zirconium alloys, which, unlike other structural materials, have a very small thermal neutron absorption cross-section (0.18 barn), which is necessary for the use of low-enriched nuclear fuel.

In the programs of work carried out in the world to improve nuclear fuel for new-generation WWER (PWR) reactors and which are aimed at further improving the operational reliability of fuel cells with fuel burn-up to 70…75 (GW·days)/t U and a campaign length of up to 6…7 years, much attention is paid to increasing the resource characteristics of zirconium fuel element cladding and components of fuel assemblies.

One of the most important requirements for the structural materials of nuclear reactor cores is their high corrosion and radiation resistances, which should ensure the reliability and safety of operation of both the reactor plant and the entire power unit as a whole. Meeting the corrosion and radiation resistance requirement is particularly important for structural materials of reactor fuel element cladding, which are made of Zr-1%Nb zirconium alloy. With a minimum wall thickness (0.65 mm), they are in the most difficult operating conditions in the core. That is, during operation, the material of fuel element cladding can deform as a result of radiation damage to the nuclear fuel in the fuel element, large thermal stresses occur in the cladding due to significant temperature changes, and the material of the cladding can change its physical and mechanical properties under the influence of neutron irradiation. Therefore, ensuring high corrosion and radiation resistance of fuel element cladding of nuclear reactors of nuclear power plants is an urgent scientific and technical problem of the world nuclear power industry [1–3].

Zirconium-based alloys has served the nuclear power industry well over a 50-year time period, and we have seen a remarkable evolution in fuel performance and reliability of such fuel cladding. However, as the current nuclear industry strive for ever higher levels of safety, productivity and efficiency, it is advisable to improve the zirconium-based alloys of fuel element cladding.

ZIRCONIUM ALLOYS FUEL CLADDING AND RELEVANT ISSUES

Zirconium alloys used in the nuclear power industry of various countries (Ukraine, Canada, USA, France, Japan, etc.) include alloys Zircaloy-2, Zircaloy-4, Zirlo, E110, E125,E635, M4, M5, MDA, and others. In the USA, Canada, and Western Europe, two main zirconium alloys are used for fuel element cladding, shrouds and channels of light-water and heavy-water reactors: Zircaloy-4 and Zircaloy-2, and the first is mainly used for fuel element reactors PWR, the second – for reactors BWR [1, 4].

In Table 1 shows the chemical composition of some zirconium alloys. These alloys, with Zr as the dominating constituent, enables a combination of desirable properties, e.g., high mechanical strength, high melting point (1852 °C, compared to, e.g., 1450 °C of stainless steel), high corrosion resistance and a low absorption cross-section for thermal neutrons. The latter is a key advantage of Zr over most other metals (in particular the main constituents of stainless steel).

All contemporary fuel cladding of water-cooled thermal neutron reactors contain 97...99% zirconium.

Minor amounts of other elements are added to optimize the desired properties, e.g., Sn, Fe, Cr, Nb, and Ni. Most of those have a low solubility in Zr, leading to the formation of precipitates, secondary phase particles (SPPs). The number density, size distribution and chemical composition of these SPPs play a major role for the inreactor performance of a cladding alloy, e.g., creep, growth, corrosion and hydrogen pickup.

Table 1

Nominal composition of some fuel cladding alloys

Cladding alloy	Nominal composition, wt.%
Zircaloy-2	Zr-1.5 Sn-0.2Fe-0.1 Cr-0.05Ni-0.12O
Zircaloy-4	Zr-(1.3…1.5)Sn-0.2Fe-0.1Cr-0.12O
E110	Zr-1Nb (O ≈ 0.05…0.07)
M5	Zr-1Nb-0.12O
E635	Zr-1Nb-1.2Sn-0.4Fe (O ≈ 0.05…0.10)
Zirlo	Zr-1Nb-1Sn-0.1Fe-0.12O

The life limit of Zr-based cladding is usually determined by its corrosion properties, i.e., oxidation in the hot reactor coolant, and in particular the associated absorption of hydrogen. At hydrogen concentrations above the limit for solid solution in Zr, zirconium hydride precipitates will form. Those have a relatively poor mechanical strength and are brittle at room temperature, meaning that excessive hydrogen can reduce the mechanical strength and ductility of cladding. Both oxidation resistance and the hydrogen pickup depend on material composition and processing as well as operating conditions, and often also change with the accumulated fast neutron fluence.

Irradiation leads to several gradual changes on the microstructural level of the material, e.g., a buildup of dislocation loops and dissolution of the secondary phase particles (SPPs), coupled to redistribution in the Zr matrix of atoms knocked out from the SPPs. These changes influence the in-reactor performance of the material, adding to the challenge of optimization.

Neutron irradiation leads to a redistribution of alloying elements between the matrix and the precipitates, and to changes in the α-solid solution composition. These changes affect accumulation and mobility of irradiation defects, anisotropy and formation of vacancy <c>-component dislocation loops. The appearance of <c>-loops usually correlates with the irradiation induced growth (IIG).

The irradiation induced growth phenomenon is a significant research area for zirconium alloys, which are used as cladding and structural materials in fuel assemblies in reactor-cores [5]. IIG refers to the volume-conservative shape change, which occurs during neutron irradiation; the cladding expands in the axial direction and shrinks in the radial direction [6]. This growth is one of the main limiting factors in the lifespan of fuel assemblies.

Irradiation-induced growth is well correlated to the evolution of dislocation loops in the material. At low fluences, irradiation-induced point defects collapse into vacancy and interstitial <a>-type dislocation loops on mostly first order prismatic planes. Upon further irradiation, <c>-component vacancy dislocation loops form on the basal plane [7].

Alloy chemistry can significantly alter the observed irradiation induced growth and particularly the point at which breakaway growth occurs. That's why, the role of Fe has been investigated with particular interest, as Fe dissolves from pre-existing second phase particles (SPPs) during irradiation and is a fast diffusing element in Zr, potentially sitting interstitially within the Zr lattice and interacting with point defects generated during irradiation [8].

In Zr-Sn, Zr-Nb and Zr-Sn-Nb alloys the addition of more Fe led to a decrease in growth strain. Also showed data from the BOR-60 test reactor, which indicated that increased Fe leads to a lower IIG strain in the Zr alloy Nb containing.

Zirconium alloys corrode relatively rapidly in steam at the elevated temperatures encountered during a design base LOCA (loss of coolant accident), e.g., caused by a large coolant pipe break. Corrosion resistance of Nb-containing alloys under normal operating conditions is excellent or superior to that of Zircaloy-4, some of them (E110 and E635) have been known to be susceptible to nodular oxidation under LOCA situations [9, 10]. High-temperature nodular oxidation leads to excessive H uptake and premature loss of post-quench ductility. In contrast, despite the fact that M5 cladding is fabricated from nominally the same type of Zr-1%Nb alloy, the alloy has been reported to be resistant to nodular oxidation under LOCA-like conditions, and neither excessive H uptake nor premature ductility loss was observed [11].

In contrast to their conventional counterparts, the modified E110 and E635 alloys fabricated using sponge Zr (Zr feedstock produced with Kroll process) performed similar to M5, and Zirlo, and were not susceptible to nodular or breakaway oxidation at high temperature in LOCA-relevant conditions [12].

Alloying elements should positively influence the corrosion resistance of products under operating conditions in the reactor and provide the necessary mechanical properties and reliability of products during operation [13, 14]. Numerous works have shown that alloying of zirconium with iron is promising in developing alloys for high temperatures. The increase of the iron content in the zirconium alloy provides the material of the cladding tubes with the required resistance to creep and strengthening under irradiation. In addition, the alloying of Zr-1%Nb alloy with iron increases its corrosion and radiation resistance in the conditions of the operation of a nuclear reactor.

However, additional alloying with iron the technological efficiency of the Zr-1%Nb alloy decreases. Therefore, determination of the optimal iron content in the Zr-1%Nb alloy is a prerequisite for providing manufacturability of the alloy and improving its operational properties.

To improve the performance properties of zirconium alloys, it is necessary to optimize the iron content (increases corrosion resistance in the coolant and resistance to radiation growth), and also use zirconium sponge as the alloys base, since such alloys meet safety criteria under LOCA conditions.

SPONGE ZIRCONIUM OBTAINING

To implement the process of obtaining sponge zirconium in Ukraine were developed a process and an apparatus for the production of metal zirconium by the reduction of zirconium tetrachloride by magnesium [15, 16].

The zirconium sponge production can roughly be divided into: chlorination of zirconium dioxide, reduction of zirconium tetrachloride to zirconium metal by Kroll process and vacuum distillation to remove impurities.

Zirconium dioxide chlorination technology was used to produce zirconium tetrachloride. The charge for chlorination was consisted of zirconium powder, zirconium dioxide, and carbonaceous reducing agent and alkali metal chlorides. After heating this mixture to a predetermined temperature, the melt was blown down with chlorine. The steam-gas mixture, which is formed and consists of vapors of zirconium tetrachloride, impurity chlorides of the accompanying metals and gaseous chlorination products, enters the condenser, where it is condensed. After the completion of the experiment obtained zirconium tetrachloride was analyzed for the content of the main impurities.

The purity of zirconium depends on the quality of the initial components (zirconium tetrachloride and magnesium), as well as on the conditions of the reduction process and on the material of the retorts in which this process is carried out. As is known, all impurities present in zirconium tetrachloride and magnesium are absorbed by zirconium.

In order to improve the quality of initial raw materials, it is necessary to carry out rectification of magnesium before loading it into the reduction reactor. And It is also to carry out sublimation purification of zirconium tetrachloride in order to obtain the minimum required impurity content regulated for obtaining reactor-grade zirconium. To protect spongy zirconium from contamination with impurities from the material of the reaction crucible, the optimal solution was proposed to apply a protective zirconium coating by the thermal diffusion deposition method. It is also extremely important to comply with the technological regulations for carrying out the processes of reduction and vacuum separation of spongy zirconium in the process of magnesium-thermal reduction.

Technological regimes for the obtaining and rectification of zirconium tetrachloride using the technology of sublimation purification have been investigated. It has been established that sublimation purification in one stage makes it possible to obtain zirconium tetrachloride with a quality sufficient to obtain reactor-grade spongy zirconium.

Processes of processing of chloride substandard products of magnesium-thermal production of zirconium by hydrolysis of zirconium chlorides with subsequent decomposition of zirconium oxychloride into high-quality zirconium dioxide ZrO_2 and processing of metallic substandard products of magnesium-thermal production of zirconium by hydrogenation and comminuting are investigated [17]. The quality of zirconium tetrachloride, obtained by processing substandard products of magnesium-thermal production of zirconium spongy, exceeds in some indicators zirconium tetrachloride, obtained by conventional technology and typical products of the world-leading manufacturers [17].

The Kroll process is very commonly used on industrial scale for the production of metals from the corresponding metal chlorides. Zirconium sponge was produced by the reduction of pure gaseous zirconium tetrachloride with molten magnesium in an inert atmosphere (by the Kroll process).

Technological regimes for the main processes of magnesium-thermal reduction from raw materials of different composition and high-temperature vacuum processing of spongy zirconium obtained under various conditions was carried out [18, 19]. The optimal temperature values in the reduction furnace and the evaporation furnace, the residual pressure in the reduction apparatus, the average loading rate and the magnesium utilization factor for the magnesium-thermal reduction process were determined. The optimal temperature values of the separation furnace, residual pressure and duration of the process for the process of vacuum sublimation (distillation) are determined.

The resulting zirconium sponge is similar in chemical composition to same from other manufacturers (for example, company ATI Metals [20]) and are according ASTM B350 data with the exception of some impurities, which has a slightly higher value (Table 2).

The method of electron-beam melting (EBM) was used to study the change in the content of impurities during the refining of a magnesium-thermal zirconium sponge of domestic production [21].

The refining processes are actively occurring during electron beam melting. Evaporation of metallic impurities is determined by the melting temperature of zirconium. Therefore impurities whose melting temperature is lower melting temperature of zirconium (Al, Ti, Cr, Mn, Fe, Ni, Cu, Ca, etc.) during electron beam melting evaporate. The content of impurities in magnesium-thermal zirconium after double electron beam melting, as well as for comparison, data for alloy Zr-1%Nb based on calcium-thermal zirconium (CTZ-110), are given in Table 2 [22].

Microstructure of obtained magnesium-thermal zirconium is similar to microstructure of iodide zirconium, microhardness is 900…1150 MPa.

Table 2

The content of impurities in the initial zirconium sponge and after double electron beam melting, wt.%
In the last columns the data for alloy Zr-1%Nb based on calcium-thermal zirconium (CTZ-110) is given for comparison

Impurity	Zirconium sponge	ASTM B350	Zr after double EBM	CTZ-110
Al	0.005…0.02	0.0075	0.0001	< 0.008
B	<0.002	0.00005	< 0.00001	< 0.00005
C	0.04	0.027	0.008	< 0.02
Co	0.0002	0.002	0.0002	< 0.02
Cr	0.01…0.02	0.02	0.00045	< 0.005
Cu	0.002…0.004	0.005	0.00002	< 0.05
Fe	0.22…0.57	0.15	0.035	< 0.01
Mg	0.05…0.25	0.002	0.25	< 0.002
Hf	< 0.01	0.01	< 0.01	< 0.005
Mn	0.002…0.003	0.005	0.00002	< 0.02
Mo	0.0025	0.0025	< 0.0005	< 0.02
Ni	0.007…0.01	0.007	0.007	< 0.007
Si	0.003…0.02	0.012	0.0006	< 0.008
Sn	<0.001	0.005	<0.001	< 0.00005
Ti	0.0035	0.005	0.0092	< 0.02

Thus, the technology of magnesium-thermal production of spongy zirconium was investigated in the following stages: chlorination of zirconium dioxide, reduction of zirconium tetrachloride to metallic zirconium using the Kroll process and vacuum distillation to remove impurities, as well as its refining by electron beam melting method.

OPTIMIZATION THE IRON CONTENT IN THE Zr-1%Nb ALLOY

Additional iron alloying of zirconium and the Zr-1%Nb alloy is promising in the development of alloys for reactors with high reliability and safety of operation, since an increase in the iron content in the zirconium alloy provides the material of the cladding tubes with the necessary creep resistance and hardening under irradiation, which ensures the design margin of stability and increases its corrosion and radiation resistance in the conditions of the nuclear reactor operation [23].

Research on the improvement of structural zirconium materials (Zr-1%Nb alloys) by optimizing the amount of the alloying element iron were carried out. The influence of the iron content in the Zr-1%Nb alloy on the corrosion, radiation and mechanical properties and microstructure of the alloy was studied.

Samples of the Zr-1%Nb alloy based on magnesium-thermal spongy zirconium containing iron from 0.012 to 0.192 wt.% with an interval of 0.03 wt.% were used for researches.

Optimization of obtaining processes of the Zr-1%Nb alloy based on magnesium-thermal zirconium by methods of electron beam and vacuum arc melting in laboratory conditions were described in detail in [21]. Pure iron refined by electron beam melting was used for microalloying the Zr-1%Nb alloy.

The properties of alloys are determined by their structural-phase state and even small changes in the composition of Zr-Nb alloys lead to significant changes due to the appearance of different types of precipitates and changes in the matrix composition [23, 24]. The kinetics of release of new phases in αzirconium is determined by the composition of the alloy, the degree of supersaturation of the solid solution α-Zr, the composition and the crystal structure of the phases. The alloying elements have a low solubility in α-zirconium (0.005...0.02% Fe, about 0.5% Nb) and are precipitated as second phase particles (SPPs) with dimensions of 50...500 nm. The composition and type of precipitates are determined by the degree of solubility of the main alloying elements of niobium and iron in α-zirconium and their total content in the alloy [23, 24].

Metallographic studies of the structure of the Zr-1%Nb alloy samples were performed using a scanning electron microscope JSM7001F with X-ray spectral analyzer INCA Energy 350. The chemical composition of the particles was studied using the X-ray spectral microanalysis.

Metallographic studies of the structure of samples of Zr-1%Nb alloy with different iron content showed that

the samples have a two-phase structure: α-matrix and second phase particles (SPPs). The additional iron alloying the Zr-1%Nb alloy leads to the appearance of precipitates the density of which increases with increasing iron content. The microstructures of Zr-1%Nb alloy samples depending on the Fe content are presented in Fig. 1.

The presence of fine βNb SPP and a small number of larger precipitates – the Laves phases $Zr(Nb, Fe)_2$ are characteristic for samples with additional Fe alloying. The concentration of Laves phases is much lower than the concentration of βNb particles. Fe alloying up to 0.162 wt.% lead to a noticeable growth of the Laves phase. The average size of the βNb SPPs is 40...50 nm. The Laves phases are slightly larger, their average size is 80...100 nm [25]. Studies have shown that the number of Laves phase precipitates significantly depends on the Fe content in the alloy. Due to the very low solubility of Fe in α-Zr, practically all of it is concentrated in the Laves phases. The study of the chemical composition of particles using the X-ray spectral microanalysis confirmed the presence of two types of SPPs. The Fe content in the matrix is 0...0.1%, Nb – 0.3...0.7%.

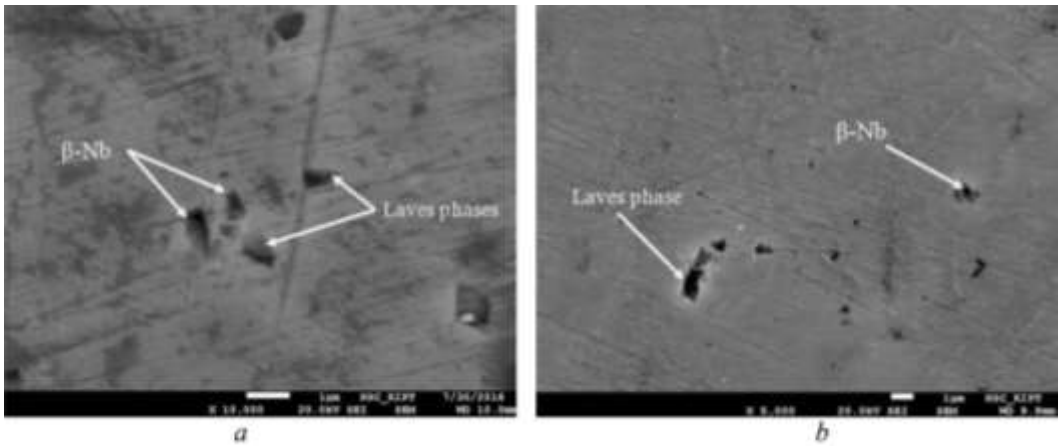

Fig. 1. The microstructure of the samples of the alloy Zr-1%Nb depending on the iron content: a – 0.072 wt.% Fe; b – 0.162 wt.% Fe

An increase in the iron content in the Zr-1%Nb alloy leads to an increase in the microhardness of the alloy. The value of microhardness for alloy samples with 0.012% Fe is 1720 MPa, for samples with 0.072...0.132% Fe – 1750...1760 MPa. And increase in the Fe iron content from 0.132 to 0.192 wt.% leads to a sharp increase in microhardness up to 1880 MPa [23].

Long-term corrosion tests of samples of the Zr-1%Nb alloy with different iron content were carried out. The study of corrosion kinetics of samples of the Zr-1%Nb alloy with different Fe content was carried out according to the methods based on the requirements of the ASTM standard [26]. The method of autoclaving was used for research, i.e. heating and corrosion tests of samples in an autoclave at a temperature of 350 °C, pressure of 16.5 MPa for a long time. Autoclaves were filled with water of a chemical composition similar to the primary coolant in reactor WWER-1000. The corrosion tests have shown that the corrosion rate of samples with different iron content is different (Fig. 2). The kinetics of weight change of samples of zirconium alloy with iron content from 0.012 to 0.162 wt.% was determined and it is shown that the additional microalloying of the alloy with iron makes a significant contribution to increasing the corrosion resistance of the Zr-1%Nb alloys [27].

For comparison of corrosion resistance we used samples made of tubes for fuel cladding from a standard alloy (E110) for a WWER-1000 with a diameter of 9.1 mm and a wall thickness of 0.65 mm. The weight gains for samples of the Zr-1%Nb alloy with content of 0.102 wt.% Fe are close to same for the standard E110 alloy or have slightly smaller values (see Fig. 2) [27]. Comparison of the surfaces of samples of both types after corrosion showed a similar character.

Processing the results of experimental studies long-term corrosion of the Zr-1%Nb alloys with different iron content by two-dimensional polynomial comb regression implemented on Python language programming based on the machine learning theory allowed determination of the optimal content of the iron alloying for the Zr-1%Nb alloy for fuel claddings.

The results of mathematical processing of experimental data obtained allow us to conclude that the dependence of the corrosion rate V (Fe, T) at a fixed T has a pronounced oneextreme character (Fig. 3), and indicates the presence of an optimal value of Fe content, which provides a minimum of the corrosion rate, and is localized around Fe = 0.1% [28, 29]. Consequently, the optimal amount of iron, which will increase the corrosion resistance of the alloy the Zr-1%Nb under operating conditions in the core of WWER-1000, it is 0.1 wt.%. Increasing or decreasing the iron content in the Zr-1%Nb alloy from the optimal amount (0.1 wt.%) leads to an increase in the corrosion rate.

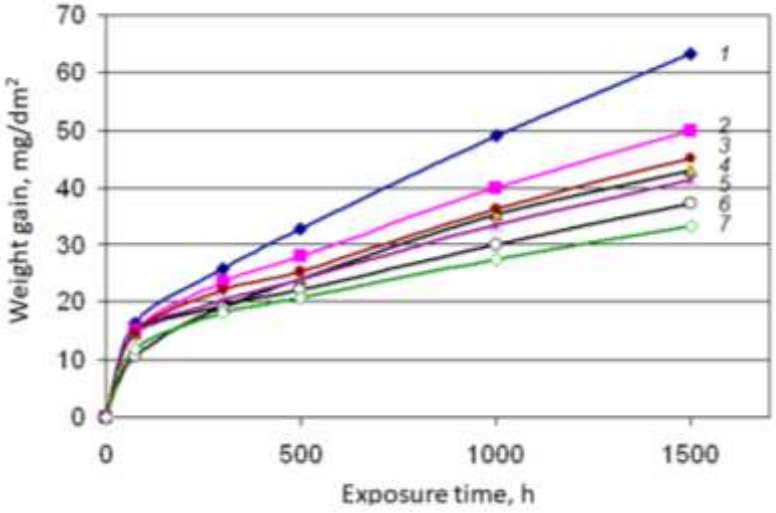

Fig. 2. Corrosion of the Zr-1%Nb alloy with different iron content:
1 – 0.012; 2 – 0.042; 3 – 0.162; 4 – 0.072; 5 – 0.132 wt.%; 6 – E-110 alloy; 7 – 0.102 wt.%

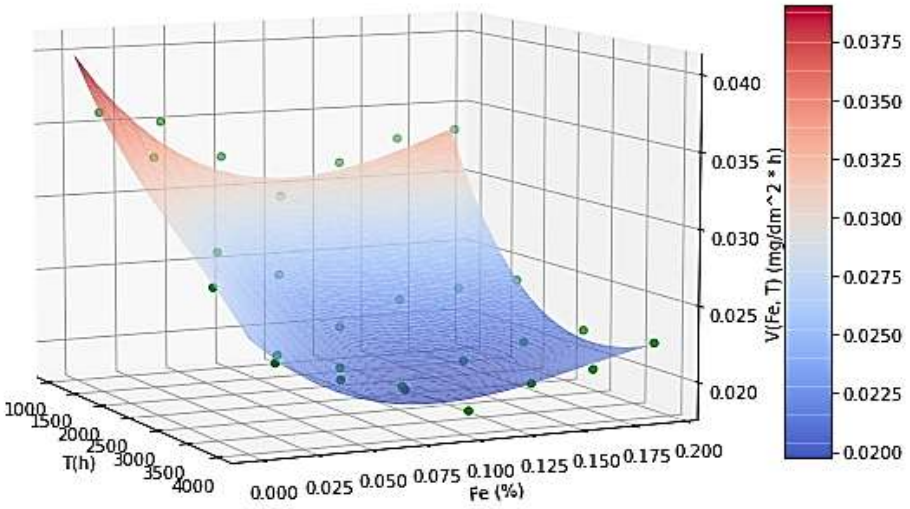

Fig. 3. The dependence of the corrosion rate V (Fe, T) at a fixed exposure time T

The Zr-1%Nb alloy with different Fe content samples were irradiated with a 1.4 MeV Ar^{2+} ion beam at irradiation temperature of 390 °C and an irradiation doses 5 and 15 displacements per atom (dpa) using the accelerating-measuring system ESU-2 [30]. The effect of irradiation with Ar^{2}+ ions on the parameters of dislocation loops in the Zr-1%Nb alloy with different Fe content was investigated by methods of transmission electron microscopy (TEM). A JEM 100 CX electron microscope was used for TEM observations of the Zr-1%Nb alloys structure before and after irradiation. The facility is equipped with a energy dispersion microanalysis system.

After irradiation in the structure of the Zr-1%Nb alloy elliptic dislocation loops of <a>-type are present. At 5 dpa the loops begin to interact with each other forming elements of dislocation network. Up to 15 dpa, only <a>-type loops are observed, <c>-type loops are not detected. Irradiation of the alloy with Fe additions leads to the formation of radiation-induced <a>-type loops and the formation of the dislocation network due to the interaction of the loops at 15 dpa [31].

Size of the loops and the loop density increases with increased the dose of damage. Data on the dependence of the size of the loops on the radiation dose are given in the Table 3.

The size of the loops decreases with increasing concentration of Fe in the alloy; the size of the loops increases with the dose of damage, and with increasing dose the growth rate of the loops decreases (tendency to saturation). This is probably due to the fact that large loops are involved in the formation of a dislocation network, and newly emerging dislocation loops make a significant contribution to the decrease in the velocity of average radius of loop with increasing dose. Consequently, the increase in the Fe concentration leads to a decrease in the size of interstitial dislocation loops and to insignificant increase in their density.

Table 3

Parameters of radiation-induced dislocation loops in the Zr-1%Nb alloys with different Fe contents

Fe content, wt.%	0.012		0.102		0.192	
Dose, dpa	5	15	5	15	5	15
Loop size, nm	22.2	28.1	19.2	26.8	17.6	25.2
Loop density, m^{-3}	$1.6 \cdot 10^{21}$	$2.1 \cdot 10^{21}$	$1.8 \cdot 10^{21}$	$2.2 \cdot 10^{21}$	$1.9 \cdot 10^{21}$	$2.3 \cdot 10^{21}$

X-ray microspectral studies of the composition of SPPs in samples of the Zr-1%Nb alloys with Fe additions after irradiation to 15 dpa showed that, the precipitates of the Laves phase contain only 1…8% Fe; the content of Fe in the precipitates of the Laves phase was 30% before irradiation. During irradiation, Fe release from the precipitates of the Laves phase, diffuse through the matrix and form secondary radiation-induced fine precipitates, which delay in <c>-type dislocation loops nucleation and leads to reduction in the radiation growth.

In accordance with the theory of anisotropic diffusion of point defects in alloys with an hcp structure [8], it can be assumed that the formation of a Fe atom-vacancy complex leads to the formation of a rapidly migration conglomerate, which rather quickly annihilates with a vacancy of atom Zr. Accelerated annihilation of the vacancy-Fe-interstitial Zr atom complex compensates for the anisotropic diffusion phenomenon and reduce the radiation growth. Therefore, we can conclude that the Fe alloying of the zirconium-niobium system alloys contributes to the suppression of the phenomenon of radiation growth in commercially effective ranges of irradiation doses.

These results may be significant to alloy design as they suggest that increasing the amount of evenly dispersed Fe-containing SPPs may be an effective way to reduce the effects of radiation growth.

CONCLUSIONS

1. The composition, properties and operating conditions of modern zirconium-based alloys fuel cladding are analyzed. The need to ensure high radiation and corrosion resistance and reliability of fuel claddings for the safe operation and higher efficiency of pressurized water reactors NPPs is substantiated. Optimization of the Fe content will lead for increases corrosion resistance in the coolant and resistance to radiation growth and using the zirconium sponge as the base of alloys provide safety criteria under LOCA conditions.

2. The technology of magnesium-thermal production of spongy zirconium on laboratory installations has been studied. The processes for obtaining spongy zirconium are considered: reduction of zirconium tetrachloride and high-temperature vacuum sublimation of the reaction mass. The change in the content of impurities during the refining of magnesium-thermal the zirconium sponge was investigated using the electron beam melting method. It is shown that the content of impurities, except for gaseous ones, in the obtained sponge and the quality of metal zirconium slightly differ from the sponge zirconium of other manufacturers. The results of the research can be used to develop an industrial magnesium-thermal technology for the production of spongy zirconium and equipment for its production.

3. The evolution of the structure of the Zr-1%Nb alloy with increasing iron content has been studied. It is shown that small additions of iron to the Zr-1%Nb alloy lead to a change in its structure due to the appearance of Laves phase precipitates. It was found that the number of Laves phase precipitates is determined by the Fe content in the alloy and increases with increasing Fe content. The microhardness of the Zr-1%Nb alloy increases with increasing iron content.

4. Long-term corrosion tests of samples of the Zr-1%Nb alloy with different iron content, obtained by Ukrainian technology, in the water environment with composition and parameters (temperature 350 °C, pressure 16.5 MPa) corresponding to the coolant of the primary circuit WWER-1000 were carried out, and mathematical processing of the results of these studies allowed us to determine the optimal Fe content. Processing the results of experimental corrosion studies made it possible to determine the optimal Fe content, which will increase the corrosion resistance of the Zr-1%Nb alloy under operating conditions in the WWER-1000 core; it is 0.1 wt.%.

5. Ar^{2+} ions irradiation of the Zr-1%Nb alloy with different Fe content showed that increasing the Fe concentration leads to the decrease in the size of the interstitial dislocation loops and a slight increase in their density. During irradiation, the Fe release from the precipitates of the Laves phase, diffuse through the matrix and form secondary radiation-induced fine precipitates, which delay in <c>-type dislocation loops nucleation responsible for the acceleration of radiation growth. The Fe alloying of the alloys of the system Zr-Nb contributes to the suppression of the phenomenon of radiation growth in commercially effective ranges of radiation doses.

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УДОСКОНАЛЕННЯ КОНСТРУКЦІЙНИХ МАТЕРІАЛІВ ДЛЯ ОБОЛОНОК ТЕПЛОВИДІЛЯЮЧИХ ЕЛЕМЕНТІВ ВІТЧИЗНЯНИХ ЯДЕРНИХ РЕАКТОРІВ

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Розглянуто покращення таких властивостей, як корозійна та радіаційна стійкість конструкційних оболонок твелів із цирконієвих сплавів для ядерних реакторів АЕС шляхом оптимізації вмісту Fe в них. Обґрунтовано необхідність забезпечення високої радіаційної та корозійної стійкості і надійності оболонок твелів для безпечної експлуатації водо-водяних реакторів АЕС в експлуатаційних умовах. Досліджено технологію магнієтермічного виробництва губчастого цирконію на лабораторних установках, оскільки використання цирконієвої губки як основи сплавів забезпечує критерії безпеки в умовах LOCA. Експериментальні дослідження показали, що оптимізація вмісту Fe у сплаві Zr-1%Nb призводить до підвищення корозійної стійкості в теплоносії та стійкості до радіаційного зростання під час опромінення. Обробка результатів експериментальних досліджень дозволила визначити оптимальний вміст Fe у сплаві Zr-1%Nb та оболонок твелів.