SECTION 2

THERMAL AND FAST REACTOR MATERIALS

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POTENTIAL MECHANISMS AFFECTING ZIRCONIUM ALLOY DEGRADATION DURING LONG-TERM DRY STORAGE

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The results of theoretical and experimental studies are considered, which determine the influence of hydrogen and hydrides on the change in the mechanical properties of the material in zirconium alloy fuel rod cladding of WWER reactors under operating conditions, during handling, technological operations and long-term storage of spent nuclear fuel (SNF).

INTRODUCTION

Hydrogen in zirconium alloy fuel cladding in WWER reactors has been a long-standing issue for the international community. The behavior of hydrogen in zirconium alloys has been studied for more than 50 years, and a large amount of experimental data has been accumulated during this period. In 2009, the Department of Energy/Office of Nuclear Energy established the Used Fuel Disposition Campaign (UFDC) to promote R&D related to the storage, handling, and disposal of spent nuclear fuel and high-level radioactive waste.

UFDC initiated monitoring of the phenomena hazardous to SNF components and storage facility structures, involving research centers that deal with SNF management issues. It was found that the phenomena and mechanisms affecting the fuel rod cladding integrity are: creep, corrosion, mechanical cracking, local and uniform damage of oxide film, defects, hydride reorientation, delayed hydride cracking, hydrogen diffusion due to temperature gradient, and embrittlement [1–5]. Hydride reorientation and hydrogen embrittlement were found to be especially dangerous for spent nuclear fuel cladding [6].

Hydrogen uptake and subsequent hydrogen-induced degradation of zirconium materials is a complex and multifactorial process. It is studied using theoretical approaches and experimentally, taking into account all technological operations. However, the published results do not give a complete picture. The lack of "unifying" theoretical models impedes analyzing the accumulated information and understanding many processes taking place in SNF cladding [5–10].

1. HYDROGEN ACCUMULATION DURING CORROSION

Most of the hydrogen in zirconium alloys is formed by the corrosion process. Most part of hydrogen dissolves in the coolant, but a part of it enters the cladding material. This part depends on the cladding material properties, cooling conditions and oxide layer thickness in the cladding. The amount of absorbed hydrogen decreases as the thickness of the oxide film increases [4].

Near the oxide-metal boundary, there is always a thin protective layer of dense ZrO_2 oxide [5–7]. Under conditions of oxidation (oxygen) deficiency, ZrO_2 begins to dissolve, resulting in local degradation of the protective layer and rapid direct interaction of hydrogen with zirconium alloys [8, 9, 11]. When zirconium alloys corrode in water or steam, the amount of oxygen that oxidizes the alloy is sufficient to maintain (restore) the diffusion barrier. When H_2O molecules dissociate, oxygen diffuses toward the oxide. Hydrogen either recombines into molecules and leaves the cladding in a gaseous state, or diffuses into metal. Competition between these processes determines the amount of hydrogen absorbed [12, 13].

Describe the importance of secondary phase inclusions [14, 15]. The authors assume that the prevailing transfer of hydrogen through oxide film containing intermetallics is caused not only by rapid diffusion, but also by the facilitated penetration of the corrosive medium through cracks and pores, which are often found near intermetallics.

The tendency of zirconium materials to absorb hydrogen depends on their composition and structure-phase state.

Investigation of the effect of oxidation level of unirradiated zirconium samples on the process of their hydrogenation showed that the peculiarities of oxide film formation in zirconium alloys of different chemical composition affect the amount of hydrogen in the alloy [16–19]. Thus, in Zirlo, having a small (up to 25 μm) oxide film thickness, the amount of hydrogen increases with increasing the film thickness [20], which is not observed in binary Zr-Nb alloys. Zircaloy-4 demonstrates linear increase in the amount of hydrogen with increasing the oxide layer thickness up to 65 μm [21].

The microstructure of zirconium alloys such as Zirlo and Zircaloy contains a large number of relatively large intermetallic compounds $Zr(Fe, Cr)_2$ and $Zr_2(Fe, Ni)$ [22, 23], which form areas accelerating alloy corrosion. This is probably why such alloys are more prone to oxidation and hydrogenation than binary alloys based on the Zr-Nb system.

2. FORMATION OF HYDRIDES IN ZIRCONIUM ALLOYS

Hydrogen easily penetrates zirconium alloys because zirconium is a metal possessing highly active chemical adsorption and absorption capacity. The hydrogen absorption process involves several stages [1]: ingress of molecular hydrogen onto the surface, accumulation of hydrogen molecules on the surface and their dissociation (physical adsorption, dissociation, and chemical adsorption (chemosorption) of hydrogen molecules), redistribution of hydrogen atoms throughout the volume (diffusion), and hydride formation upon reaching the hydrogen solubility limit.

Hydrides, in turn, are realized in various configurations in practice [1]:

- at grain boundaries and within grains (intergranular and transgranular);
- along grain boundaries and perpendicular to them;
- with extensions into neighboring grains;
- hydrides that cross the entire grain, small hydrides scattered in the grain.

Formation of hydride structures in the process of dry storage

During dry storage, various types of hydrides are formed, as shown in Fig. 1 [1]:

- with alow hydrogen content and rapid cooling (at a rate of 10 °C/min and above, γ-hydrides are formed);
- with cooling rates ranging from 2 to 10 °C/min, both γ- and δ-hydrides are formed;
- with a cooling rate below 2 °C/min, only δ-hydrides are formed;
- γ- and ε-hydrides are also present (along with δ- and ζ-hydrides) in areas of local hydrogen concentration (typically formed along the external surface of Zircaloy-2 and Zircaloy-4 cladding during operation).

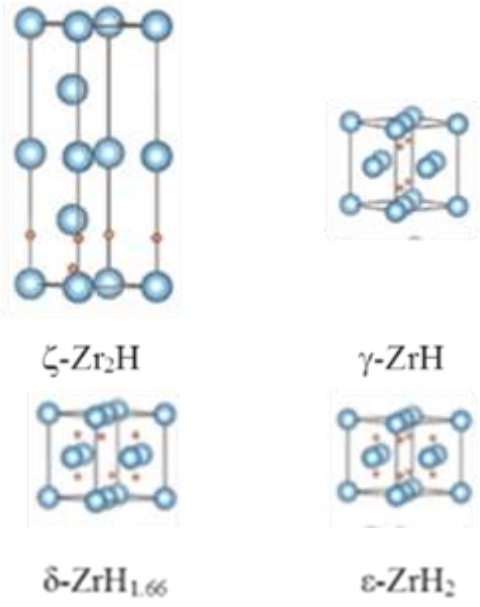


Fig. 1. Crystal lattices of various hydride types in zirconium alloys [1]

Types of hydrides and their crystal lattices formed in fuel rod claddings made of zirconium alloys are given in Table.

In zirconium alloys, gradual hydrogen saturation to a concentration of 300…1000 ppm results in formation of non-stoichiometric δ-ZrH_{2-y}. It is a hydride with a typical H/M ratio of ~ 1.66, having a face-centered cubic lattice (FCC, CaF_2 type, a = 0.4768 nm, V_e = $108.39 \cdot 10^{-3}$ nm^3 [4, 5].

Types of hydrides and their crystal lattices formed in fuel rod claddings made of zirconium alloys [24]

Hydride type	Crystal lattice	Lattice parameters, A	Composition
δ	FCC (face-centered cubic lattice)	a = 4.778	$ZrH_{1.3\text{-}1.7}$
γ	HCP (hexagonal close-packed lattice)	a = 4.596 c = 4.969	ZrH
ζ	HCP (hexagonal close-packed lattice) (trigonal)	a = 3,3 c = 10,29	$Zr_{2\text{-}4H}$
ε	HCP (hexagonal close-packed lattice)	a = 4.969 c = 4.45	$ZrH_{1.7–2}$

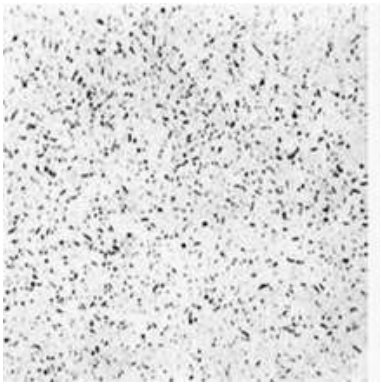
Under certain conditions (low hydrogen content, slow cooling (below 2 °C/min), long-term exposure to low temperatures (e.g., room temperature)), a metastable phase γ-ZrH may be formed in zirconium alloys with a tetragonal lattice (BCC, $P4_2/n$, a = 0.4586 nm, c = 0.4948 nm), in which hydrogen atoms occupy four tetragonal positions on the (110) planes alternating with the planes of Zr atoms. Zr atoms are located at positions (0.25; 0.25; 0.25), H atoms are located at positions (0; 0; 0) and (0; 0; 0.5) [5, 6].

Information on planes where hydrides precipitate differs significantly: $\{10\bar{1}0\}$, twinning planes $\{10\bar{1}2\}$, $\{11\bar{2}\bar{1}\}$, $\{11\bar{2}\bar{2}\}$, pyramidal planes $\{10\bar{1}1\}$, basal planes (0001) and $\{10\bar{1}\bar{7}\}$ [23–25]. This inconsistency in results is not related to difficulties in determining the planes of hydride precipitation and the orientation relationship between hydride and matrix. It reflects the true picture of what happens. The dependence of the planes of hydride precipitation on the texture, structure, stress state, and manufacturing and thermal treatment technology determines the initial hydride type.

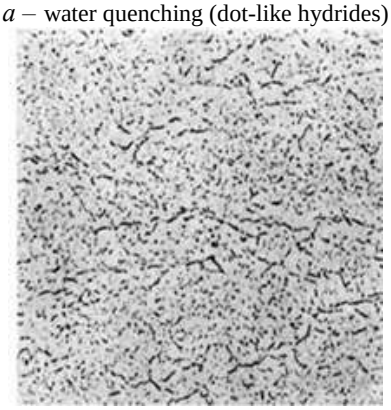
The habit planes $\{10\bar{1}\bar{7}\}$ and (0001) are typical for cladding and channel tubes, and the orientation relationship between δ-hydride and α-matrix is $\{111\}\delta \| (0002)\alpha$ and $\langle \bar{1}10\rangle\delta \| \langle 11\bar{2}0\rangle\alpha$, which is accepted in their manufacturing practice [7].

Fig. 2 shows hydride morphology: a, b – after operation, fuel is transferred to a spent fuel pool with the water temperature of 50…70 °C, which promotes

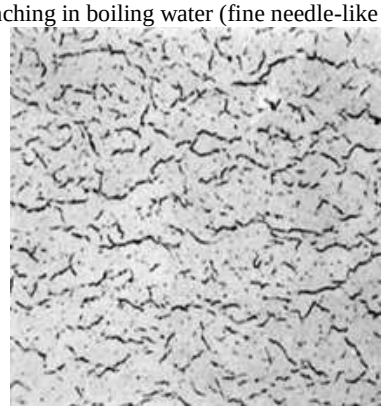
formation of a hydride structure in the cladding characteristic of hardening. This structure does not pose a risk in terms of degradation of mechanical properties, as hydrides are represented by randomly oriented needles several tens of micrometers long, evenly distributed across the cladding cross-section.



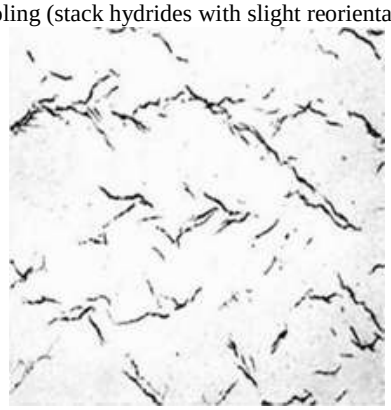
a – water quenching (dot-like hydrides)



b – quenching in boiling water (fine needle-like hydrides)



c – air cooling (stack hydrides with slight reorientation)



d – furnace cooling (more noticeable stack hydrides, with significant reorientation)

Fig. 2. Hydride morphology [24]

Fig. 2,c and d show the subsequent stage (a multi-stage SNF management process) – vacuum drying, which involves a temperature gradient that can result in dissolution and precipitation of hydrides. The maximum cladding temperature plays a key role here, as it determines how much hydrogen will be involved in the reformation of hydrides [24].

At the final stage of SNF storage, cooling is performed in sealed containers, where the fuel rod cladding temperature is gradually decreased from the maximum values at cooling rates sufficient for the complete passage of diffusion processes. The hydride structure is characterized by long stacks up to hundreds of micrometers in length, the density of which is determined by the amount of hydrogen.

When sufficiently high stresses are applied, hydride platelet formation takes place primarily in the direction perpendicular to the stress direction, which ensures maximum stress relaxation in the matrix.

This is why the defects caused by hydrogenation, especially radially-oriented hydrides, are considered dangerous during long-term storage of spent fuel rods. Reformation of hydrides under stress conditions at elevated temperatures and potential thermal cycles is also dangerous.

The type of hydride phase depends on the initial type of hydride and its amount in the fuel rod cladding, which will affect the structure-phase state and behavior of zirconium alloy cladding under dry storage conditions. [1, 24]

3. MECHANICAL CRACKING, LOCAL AND UNIFORM DAMAGE OF OXIDE FILM

Hydrogen, penetrating inside the cladding, continues its movement within the zirconium matrix under the action of several driving forces. During operation, hydrogen redistributes within the cladding in accordance with the diffusion equation. Under the influence of such forces, hydrogen tends to move into areas of increased tensile stress, colder areas, and lower concentration areas. The concentration gradient causes hydrogen to diffuse from external to internal surface of the cladding (Fick's diffusion). During reactor operation and long-term dry storage, the temperature gradient in fuel rod claddings is oriented toward the internal wall (where the fuel pellet is located), which promotes hydrogen diffusion towards the external surface. At the same time, the temperature gradient across the wall thickness during reactor operation at rated power is about 20…30 °C [25–27].

To increase heat transfer from fuel pellets to cladding, for tightness control, reduction of gaseous fission products (GFP) release, and prevention of cladding collapse, the internal space is filled with helium (up to a pressure of 2…2.5 MPa for WWER-1000). At operating temperature, the gas pressure increases by approximately 2 times.

Helium is an inert gas that is insoluble in metals. It is released at grain boundaries in the form of bubbles, weakening these boundaries and reducing plasticity. Helium can cause mechanical cracking of the oxide film in zirconium alloys, both local and uniform.

By the end of a fuel cycle, a sufficient amount of uranium fission fragments is accumulated, of which approximately 5% are GFRs. As a result of the combined action of helium, GPR, and swelling fuel pellets, tensile stress fields are formed in the cladding [27, 28]. During operation, tensile stresses are compensated by the external coolant pressure (approximately 15.5 MPa), while compressive stresses are created in the cladding. However, during dry storage, due to the absence of external coolant pressure, only the internal pressure factors are present. In this case, a tensile stress gradient is created across the wall thickness, directed towards the internal surface, which in turn promotes the movement of hydrogen towards the internal cladding surface. Additionally, hydrogen diffusion under tensile stresses is the reason for one of the most dangerous mechanisms of zirconium alloy embrittlement – delayed hydride cracking (DHC) [28].

4. DELAYED HYDRIDE CRACKING

Diffusion accumulation of hydrogen in low-temperature and increased tensile stress areas leads to embrittlement and subsequent destruction of products by the delayed hydride cracking mechanism. Hydrogen atoms deform the crystal lattice leading to elastic (deformation) interaction between hydrogen atoms and alloy. At close distances, on the order of atomic distances, chemical repulsion forces prevail. At large distances, hydrogen atoms attract each other. This interaction is highly dependent on temperature and hydrogen concentration [27].

For the first time, such cracking phenomena with formation of penetrating cracks in pressurized cladding were observed during operation in CANDU [23, 24] and RBMK [25] channel-type reactors. Cracking of circalloy fuel cladding in boiling water reactors (BWR) is also associated with DHC [26–32]. The most pronounced cladding cracking in BWR reactors occurred with formation of long penetrating cracks in the axial direction (axial cracks) [26–31]. As a result, the content of uranium and its decay products in reactor core water increased, causing radiation safety violations at nuclear power plants (NPPs) [26–28]. A penetrating crack in the radial direction, originating from the external surface of the cladding, was also observed in a fuel rod with high burnup during power ramp-up in BWR reactors [32]. Thus, the DHC phenomenon must be taken into account when developing fuel rods to substantiate the operating performance of the cladding material in transient modes. In addition, DHC is also considered a potential mechanism for cladding degradation during dry storage of spent nuclear fuel [2, 33, 31].

Currently, zirconium alloys with various alloying elements are used as the cladding material for water-cooled nuclear reactors. The most widely used systems are Zr-Nb (alloys E110 and M5), Zr-Sn-Fe, and Zr-Nb-Sn-Fe (alloys E635 and ZIRLO). In addition to different concentrations of alloying elements, zirconium cladding can have different solid solution compositions, types of secondary phase precipitates, and structural states after final heat treatment. Alloying and microstructure control material strength and fracture toughness, which affects the DHC kinetics. This effect was confirmed by the tests, which evaluated the influence of zirconium alloy strength on crack growth rate in DHC tests: the lower the strength, the lower the crack growth rate [33–38]. In DHC tests performed on low-strength claddings, it is difficult to initiate hydrogen cracking and prevent crack arrest due to tip blunting.

To date, there is a lot of well-founded and experimentally confirmed data on the DHC parameters for Zircaloy-4 fuel cladding obtained by participants in IAEA projects using approved testing methods [31, 36, 37, 39]. For zirconium alloys of other alloying systems – Zr-Nb, Zr-Sn-Fe, and Zr-Nb-Sn-Fe – such data are fragmentary [39, 40] or completely absent.

The study [41] presents investigations of DHC parameters and their temperature dependencies for tube claddings made of three zirconium alloys representing different alloying systems – Zr-Nb, Zr-Sn-Fe, and Zr-Nb-Sn-Fe – with the aim of comparing their resistance to this damage mechanism.

The samples used in their study were tube claddings with an outer diameter of 9.5 mm and a wall thickness of 0.57 mm, made of Zircaloy-4, E635M, and $E110_{opt}$ alloys. The tubes were made of a material produced using the Kroll process to create a zirconium sponge.

Zircaloy-4, manufactured by Sandvik, was also tested by the authors as part of their participation in the IAEA project in 2011–2015 [39]. The final annealing mode for the Zircaloy-4 tube was 480 °C for 3.5 h, which provides the SFA state for which DHC parameters were previously demonstrated in tests [31, 36, 37, 39].

$E110_{opt}$ is the main material for thin-walled fuel claddings with increased uranium content in WWER reactors [42], and is also undergoing pilot-commercial operation as a TVS-K fuel cladding for PWR reactor at Ringhals NPP [43]. E635M, as a fuel rod cladding material for pilot WWER-1000 FAs, was used at the Balakovo NPP Unit No. 2 for three 18-month cycles until fuel burnup reached about 60 (MW·h)/kgU [44]. Besides, E635M, just like $E110_{opt}$, was tested as a cladding material for experimental PWR fuel rods at the Halden reactor using a water chemistry with a lithium content of 10 ppm [45]. Tubes made of $E110_{opt}$ and E635M alloys during fuel rod cladding manufacturing are annealed to the RXA condition. Since the mechanical strength of such tubes is quite low, it is impossible to initiate hydrogen cracking during DHC tests due to blunting of the fatigue crack tip during loading or after long-term sample exposure to load. Therefore, for experiments with DHC, tubes made of $E110_{opt}$ and E635M were annealed at 400 °C for 24 h after final rolling to relieve stresses, while retaining strain hardening. The strength of the tubes in this condition increases by 1.6…2.1 times depending on the test temperature, while the structural condition and texture of the tubes are similar to those of Zircaloy-4 tubes (see Table). The tubes of the three alloys had a single-phase α-Zr matrix with elongated, deformed grains and a secondary phase that precipitates as β-Nb particles or intermetallics distributed in the matrix.

Another factor determining the degree of embrittlement is hydrides formed in zirconium alloys

upon reaching the hydrogen solubility limit (type γ, δ, ε) [1–5]. Hydrides oriented perpendicular to the tensile stress (radial hydrides) also lead to significant embrittlement of zirconium alloy cladding. Therefore, when manufacturing cladding tubes from zirconium alloys, conditions are created that are suitable to form hydrides with a "favorable" tangential orientation.

5. HYDRIDE REORIENTATION IN FUEL ROD CLADDINGS UNDER CONDITIONS OF THEIR STORAGE IN SFDSF

Hydrides tend to redistribute in the direction perpendicular to the tensile stress when a Zr sample is cooled under stress from a temperature at which the hydrides dissolve. This is called hydride reorientation [71]. As a rule, for zirconium tubes, hydrides formed at zero stress (during the cladding manufacturing process) are called tangential hydrides, and reoriented hydrides are called radial hydrides, as shown in Fig. 3,a,b. A radial hydride returns to an annular hydride after stress relief annealing, which means that tensile stress is a key factor causing hydride reorientation [72–74].

Zirconium alloys for fuel claddings are manufactured in such a way as to promote hydride precipitation in the tangential direction. However, under certain temperature and stress conditions, hydrogen can dissolve and be released in the radial direction. The degree of reorientation depends on several parameters, such as internal pressure, maximum temperature, cooling rate, thermal cycles, amount of undissolved hydrides, and texture [56–68].

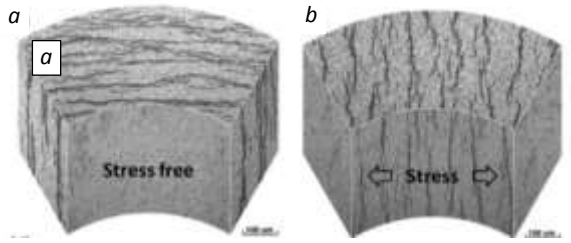
Hydride reorientation during cooling under internal pressure and its effect on ductility have been widely studied in unirradiated and irradiated fuel rods made of various types of zirconium alloys, such as Zircaloy-2 (Zry-2), Zircaloy-4, ZIRLO, and M5 [1–6] . Several more studies have recently been conducted to investigate the effect of hydride reorientation on the ductility of fuel rods.

One such study was conducted at NFC STE and presented in [98]. The study describes the effect of hydride reorientation on internal pressure under the cladding, different temperatures, cooling rates, thermal cycling, and the amount of hydrogen in the cladding. For the study, an unirradiated E110 alloy was selected with stresses in the cladding below 80 MPa and cooling temperatures of 410 and 450 °C with a cooling rate of 2...4 °C/min; its structure-phase state and test conditions are described in [69].

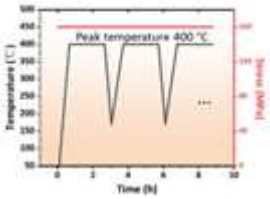
Aomi et al. [59] studied irradiated and unirradiated Zircaloy-2 (Zry-2), ZIRLO, and M5 at the cladding stresses below 70 MPa during cooling from the temperatures of 300 and 400 °C at a cooling rate of 30 °C/h. A study by Aomi et al.[59] showed that when the temperature was reduced from 400 to 300 °C at cladding stresses below 70 MPa, the amount of radial hydrides decreased. Furthermore, when the cooling rate decreased from 30 to 0.6 °C/h, all hydrogen diffused into the external part of the cladding, leaving the internal part completely depleted of hydrides.

Auzoux et al. [60] obtained similar results while studying reorientation in similar alloys. They found that during cooling from 400 °C at a cooling rate of 60 °C/h, reorientation of hydrides occurs at effective stresses between 40 and 80 MPa in unirradiated claddings and below 40 MPa in irradiated samples. Despite the significant hydride reorientation, unirradiated samples retained high plasticity (> 15%) during tensile testing. This is due to the low yield strength of the matrix and the hydrogen-depleted zone towards the external part. The irradiated cladding was less ductile. However, when the cooling rate decreased from 60 to 0.6 °C/h, ductility was restored, as almost all the hydrogen was released into the outer part of the cladding.

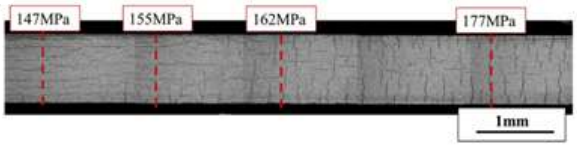
The overall conclusion from the earlier studies [56–61] of fuel rod claddings is that, given enough time for hydrogen to diffuse into the cladding, the amount of hydrogen remaining inside the cladding is not sufficient to cause any harmful reorientation of hydrides. However, these studies focused on claddings under stresses of less than 70 MPa and with hydrogen content of up to 300 ppm.



a – Tangential hydride; b – radial hydride formed after 8 treatment cycles at 400 °C (peak temperature)



c – Sample heat treatment graph [17]



d – Hydride distribution in the cross section of a conical uniaxial tensile specimen after 2 thermal cycles [75]

Fig. 3. Types of hydrides during thermal cycling

In [69], it was determined that at cladding stresses of σ_θ=44…76 MPa, tests at temperatures of 410, 450 °C, holding for 8 h, and subsequent cooling at a rate of (120 °C/h) result in insignificant reorientation of hydrides in claddings with a hydrogen content of up to 150 ppm. Structural studies demonstrated that with a hydrogen content exceeding 170 ppm and tangential stresses in the fuel rod claddings ≥ 56 MPa, hydride reorientation occurs. When the hydrogen content in the fuel element cladding exceeds 200 ppm, the process of hydride reorientation begins at lower tensile stresses. Three thermal cycles 300↔450 °C and 180↔450 °C of fuel rod dummies with a tangential stress in the cladding of $\sigma_\theta \geq$ 56 significantly increase the level of hydride reorientation. Increasing the number of cycles 300↔450 °C from 3 to 5 and further to 7, causes an

additional increase in the degree of hydride reorientation (up to 0.98 after 7 thermal cycles in claddings with a hydrogen content of 400 ppm). Three thermal cycles 180↔450 °C increase the degree of hydride reorientation to 0.89 (in claddings with a hydrogen content of 400 ppm); increasing the number of cycles 180↔450 °C from 3 to 7 does not cause additional increase in the degree of hydride reorientation.

All the data obtained show that temperature conditions, stresses in the cladding, and external factors affect hydrogen migration in the cladding, hydride redistribution and reorientation.

CONCLUSIONS

The amount of hydrogen and its subsequent reorientation pose a particular danger to spent nuclear fuel cladding. The tendency of zirconium materials to absorb hydrogen depends on their composition and structure-phase state.

The main factors affecting changes in the structure-phase state are circumferential stress, temperature conditions, hydrogen content, and type of hydride phase in cladding materials.

When studying the hydride phase behavior, it is necessary to take into account the history of formation, mechanisms, and environment of fuel element cladding materials for each alloy separately.

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ПОТЕНЦІЙНІ МЕХАНІЗМИ, ЩО ВПЛИВАЮТЬ НА ДЕГРАДАЦІЮ ЦИРКОНІЄВИХ СПЛАВІВ ПІД ЧАС ТРИВАЛОГО ЗБЕРІГАННЯ В СУХОМУ ПРИМІЩЕННІ

Ганна Редкина

Розглянуто результати теоретичних та експериментальних досліджень, які визначають вплив водню та гідридів на зміну механічних властивостей матеріалу в оболонці твелів із цирконієвого сплаву реакторів ВВЕР у експлуатаційних умовах, під час маніпуляцій, технологічних операцій та тривалого зберігання відпрацьованого ядерного палива (ВЯП).