Structural features of hydrogenated E110opt and E635 tubes

M. G. Isaenkova, Professor1, Doctor of Physical and Mathematical Sciences, e-mail: MGisaenkova@mephi.ru
M. I. Petrov, Engineer1, e-mail: mipetrov.99@yandex.ru
I. V. Kozlov, Engineer1, e-mail: ilya_mephi@mail.ru
A. V. Bogomolova, Engineer4, e-mail: bogomolova@m-a-l.ru

1National Research Nuclear University “MEPhI”

The paper investigates the behavior of the hydride phase in hydrogenated tubes made of Russian zirconium E635 and E110opt alloys. The orientation and fraction of mesoscale hydrides in the alloy matrix have been described by analyzing optical metallographic images using the developed software. Metallographic images were used to assess the predominant orientation of hydrides in the axial section of the tube, as well as the surface density of the hydride phase with an increase in the concentration of hydrogen in tubes made of different alloys. It has been shown that increasing the hydrogen concentration to 600–700 wppm increases the number of radially oriented hydrides, which is associated with the development of compressive radial stress during the formation of tangentially oriented hydrides at the initial stage. Increasing the hydrogen concentration in E110opt alloy cladding tubes to 600–700 wppm leads to a change in the orientation of the α–zirconium basal axes, which results in an increase in the integral textural $t_{\alpha}$-parameter and a decrease in the $t_{\gamma}$- and $t_{\beta}$-parameters. This change is due to the development of radial compressive stress and is only possible due to the activation of twinning in the grains, the basal axes of which are deflected from the compressive stress at an angle of up to 90 degrees.

The results of synchrotron Debye rings and X-ray reflection diffraction analysis revealed patterns of structure and texture formation of zirconium matrix and hydrides with increasing hydrogen concentration in E110opt and E635 tube materials. Twinning by the (1012) (1011) and (1011) (1012) systems has been detected in the alloy E110opt. It reorients the basal axes at angles of 85° and 57.2° in the direction of compressive stress applied in the radial direction. According to the crystal lattice geometry of the α-phase, this reorientation occurs in the direction deviated from the radial direction by 30 degrees. It has been established that in E635 alloy hydrides with (001) (110) orientation are predominantly formed, but hydrides with additional (110) (011) and (110) (112) orientations are also present in smaller amounts. In the E110opt alloy there are hydrides of (001) (110) and (110) (011) orientations as well as (112) in approximately equal proportions. The presence of hydrides with a (112) partially axial textural component is due to activation in the α-phase of twinning along the (1012) and (1011) planes, in which hydrides are formed according to the established orientation relationship (0001)$_{\alpha}$ $\rightarrow$ Zr [111]$_{\alpha}$ $\rightarrow$ ZrH$_{1.8}$.

Key words: zirconium alloys, hydrides orientation, microstructure, crystallographic texture, X-ray, synchrotron radiation, orientation relationship.

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1. Introduction

Zirconium alloys combine high mechanical properties, corrosion resistance, and low neutron absorption cross-section [1–4]. Therefore, they are used for the manufacture of structural elements and nuclear fuel cladding of the core of VVER nuclear reactors. Hydrogen is among the causes of embrittlement of structural materials in modern nuclear reactors, leading to reduction of service life of their structural elements [5–8]. In the nuclear reactor core, fuel elements such as the fuel rod cladding, spacer grids, angles, guide channels, and so on are exposed to thermal and mechanical stress that can cause deformation of components, neutron flux that causes radiation damage, and chemical effects of coolant that lead to material corrosion and hydrogenation.

Zr alloys oxidize slowly and uniformly due to the reaction of the outer surface of the product material with cooling water. This produces a corrosion protection layer consisting mainly of monocline zirconium dioxide, according to the reaction: Zr + 2H$_2$O $\rightarrow$ ZrO$_2$ + 2H$_2$. [9–10]. The source of hydrogen which is of most concern is the trapping of hydrogen by the zirconium alloy cladding during this reaction. As argued in [11], only hydrogen from corrosion enters the cladding, although there are other sources of hydrogen (e.g., radiolysis of water). When the content of hydrogen dissolved in Zr alloys exceeds its solubility limit in the solid state, zirconium hydrides precipitate as lenticular plates [7–12]. Hydride formation can significantly degrade mechanical properties of the materials, which leads to a decrease in both ductility and fracture toughness [13–19].

One manifestation of the influence of hydrogen on the behavior of zirconium products, especially channel tubes made of Zr – 2.5% Nb alloy, is the delayed hydride cracking (DHC) developing under cyclic loading conditions and described in detail in papers [20–21]. At the same time, hydride cracking of cladding tubes during their operation for 2.5–3 years did not occur. However, at present,
due to the increase in the service life of fuel rods from three to five years and subsequent transportation and storage of spent fuel, the relevance of the hydride topic is also increasing. Fuel burnup and, consequently, neutron fluence and increased hydrogen concentration in the material are increasing, which leads to changes in its microstructure, including an increase in the density of dislocation loops and the dissolution and re-emission of both intermetallic particles [22, 23] and hydrides. These microstructural changes can degrade the cladding tube characteristics due to variations in mechanical properties (hardening, embrittlement, loss of fracture toughness), dimensional variations associated with irradiation-induced deformation (creep and growth), and changes in corrosion resistance.

It is known [22, 23] that radiation damage-related hardening and embrittlement reach saturation after one month in the reactor. A potentially major concern is the corrosion of the cladding tube during interaction with reactor coolant water and the resulting hydrogen intrusion into the zirconium cladding (hydrogen pickup) that occurs during reactor operation.

It was shown in [24, 25] that the rate of DHC depends on the crystallographic texture and decreases linearly with increasing values of the $f_R/f_T$ ratio in logarithmic coordinates regardless of the alloy composition and structure (as well as in the case of the yield strength), where $f_R$ and $f_T$ are integral Kearns textural parameters that characterize the projection of the basal axes of the grain structure to the external directions in the tube: radial $R$ and tangential $T$.

The prospect of dry storage of spent fuel assemblies implies a long, well beyond service life, duration of zirconium alloy resistance to the harmful effects of hydrogen. An understanding of the mechanisms and patterns of hydride formation and growth during hydrogenation is necessary to assess the alloys' ability to resist this impact.

The foreign literature presents a great number of studies on the structure and morphology of hydride phases [9, 10, 26–39], their orientation depending on the crystallographic texture, as well as reorientation under the influence of external stress. However, most of the studies were carried out for products made of alloys of Zircaloy or Zr–2.5% Nb, annealed after 20% cold rolling at 400 ºC for 24 hours (according to the technology for obtaining tubes for the CANDU reactor). Russian alloys differ significantly in both structure and properties, which precludes their differences with respect to hydride formation [40, 41]. Thus, the study [41] demonstrated a difference in the enthalpy of hydride formation in the E110opt and E635 alloys. The results of differential scanning calorimetry showed that E110opt alloy has higher value of enthalpy of hydride precipitation $\Delta H_p$ compared to other alloys such as Excel and Zircaloy-4. E635 alloy is close to the foreign Zircaloy-4 alloy by this parameter and both of them are higher than in Excel and Zr-2.5Nb alloys in which the problem of DHC has been most acute [9, 20, 21].

In [40] it has been shown that in the E110 alloy shorter hydrides are formed compared to the Zircaloy-4 and Zr–2.5% Nb alloys, which may also be associated with a higher value of the enthalpy of hydride precipitation $\Delta H_p$ and that for the Zircaloy-4 and Zr–2.5Nb one orientation relationship (0001)$_a$–Zr $\parallel$ (111)$_b$–ZrH$_{1.66}$ is performed, and for the Zr–1 Nb (E110) alloy in addition to the indicated for about half of the grains the relationship (0001)$_a$–Zr $\parallel$ (100)$_b$–ZrH$_{1.66}$ is performed. The presence of tension twins {1012}($10\bar{1}1$) and compression twins {1011}($10\bar{1}2$) in alloy E110, which were not observed in alloy Zircaloy-4 and Zr-2.5Nb has also been noticed in the paper.

Therefore, the purpose of this study is to organize the numerous data and identify the main patterns of structure changes in E635 and E110opt Russian alloys when the hydrogen concentration increases in the absence of external stress.

2. Samples and methods of their investigation

The study was carried out on the tubes of length (35±1) mm which were cut from the fuel cladding with diameter $\phi$ 9.17x7.93 mm of E110opt alloy (Zr–1 Nb – 0.06 Fe – 0.08 O, wt.%) characterized by complete recrystallization of material, and guide channel $\phi$ 12.6x10.9 mm from alloy E635 (Zr–1 Nb – 1.2 Sn – 0.35 Fe – 0.08 O, wt.%), being in partial recrystallized state. The samples were saturated with hydrogen to concentrations of 40 to 700 wt ppm by hydrogenation from the gas phase at a fixed temperature in the range of 400–550 ºC, depending on the calculated hydrogen concentration. After hydrogenation, the actually achieved hydrogen concentrations were measured with LECO for two 2 mm high rings cut from the top and bottom of the branch tube. The average value of the hydrogen concentrations measured for the two rings is used further as the concentration for the branch tube in question.

The following research methods have been used in this study: metallographic analysis, X-ray diffraction phase analysis and analysis of the structural state of phases by X-ray line profile [42], textural analysis by diffractometric imaging [43–45] and Debye rings obtained by transmission of 120-150 μm thick foil at synchrotron radiation [46–47]. Different cross sections of hydrogenated tubes were fabricated for the methods used. The sections are further denoted by the name of their normals to their plane, parallel to the main directions in the tube: $K$–radial; $T$–tangential; $L$–longitudinal or axial.

So, for metallographic analysis, 4 mm high rings were cut using precision electrospark cutting with 200 μm thick wire. Samples have been cut into two semi-rings strictly along the diameter to obtain a section perpendicular to the tangential direction, i.e., a $T$-section. The second half-ring has been used to prepare an $L$-section perpendicular to the longitudinal direction of the tube.

The microstructure of the samples has been examined using a MIM-7 metallographic microscope. In the Russian literature, the coefficient $f_R/1$, equal to the ratio of the total length of the hydrides forming an angle less than 45° with the radial direction to the total length of all
hydrides, is used to describe the pattern of preferential orientation of the hydrides. In foreign literature, the RHC coefficient is used as such a parameter [10, 19], for the calculation of which hydrides are divided into 3 categories according to the angle they form with the tangential direction: “in-plane” (in-plane hydrides coefficient – IHC) – (0°±40°), “out-of-plane” (OHC) – (65°±90°) and “mixed” (MHC) – (40°±65°). For each of the categories, the ratio of hydrides normalized to length is determined. Thus, the RHC coefficient is:

\[ RHC = 0.5 \cdot MHC + OHC. \]

Using the developed software, the metallographic images were analyzed, which resulted in the calculation of \( F_n \) and RHC coefficients describing the preferential orientation of hydrides.

The errors were estimated as follows: each image was divided into 4 fragments and the hydride orientation coefficients \( F_n \) and RHC described above were calculated for each fragment. The difference in the results is due to the heterogeneity of the hydride distribution over the cross section of the sample, as well as to the fact that the determination of the tube contours is associated with the error arising from the approximation of the tube contours by arcs of circles. The coefficient measurement error is \( \delta(F_n) = 24\% \) and \( \delta(RHC) = 28\% \).

X-ray analysis of the structure and texture of the zirconium matrix and hydride phases was performed using synchrotron radiation with a wavelength of 0.74 Å and filtered copper radiation with a wavelength of 1.54 Å. Synchrotron studies were carried out at the “KISI-Kurchatov” facility. The transmission imaging of thin rings of 100–120 μm thickness was used. Registration of Debye rings was carried out on a 2D-detector. The summation of intensity of reflection along a circle allows to carry out quantitative phase analysis. Moreover, it is possible to reconstruct direct pole figures (DPF) for all phases presented in the material by the registered Debye rings [44]. Conventional X-ray structure and texture analysis of the samples has been performed on D8 Discover, DRON-3 and DRON-3M X-ray diffractometers using Cu \( K_\alpha \) and Cr \( K_\beta \)-radiation. Recording of diffraction spectra to determine the phase composition of the samples and assess their structural state has been carried out on a Bruker D8 Discover diffractometer using Cu \( K_\alpha \)-radiation and a position-sensitive LynxEye detector. The imaging was performed with a step of 0.01° Bragg angle of 20 and an accumulation of 0.5 s per detector strip, which gives a total of about 96 s per point. The BrukerAXS DIFFRAC.EVA v4.2 software and the international ICDD PDF-2 database were used for phase identification.

The crystallographic texture has been determined from the DPFs. The initial incomplete DPFs were used to reconstruct the orientation distribution function (ODF) [45, 46] with subsequent construction of full DPF(0001) and calculation of the integral Kearns parameters for the hexagonal phase \( \alpha \)-Zr.

3. Experimental results

3.1. Microstructure of hydrogenated zirconium tubes

Fig. 1 shows optical images for three mutually perpendicular tube sections (\( R, I, L \)) of a typical hydrogenated sample.

The metallographic images obtained for the \( L \)-section are used to estimate the hydride orientation with respect to the \( R \)- and \( T \)-directions. Fig. 2 shows plots of the dependences of the \( F_n \) and RHC coefficients on the hydrogen content for the two alloys. The plots are approximated to a straight line by the Pearson method (\( \chi^2 \) minimum), since the measurement errors differ for each point. The graphs show a linear increase in both coefficients, i.e., an increase in the number of hydrides oriented radially with increasing hydrogen concentration in the material.

3.2. X-ray phase analysis of the investigated tubes

Fig. 3 shows the change in X-ray spectra recorded using synchrotron radiation. The spectra are recalculated to the wavelength of copper radiation for the convenience of subsequent comparison with the diffraction spectra obtained on the copper radiation of the X-ray diffractometer.
In the case of recording Debye rings on synchrotron radiation, the intensity along them is summed, so the presented spectra are not influenced by the texture. Using synchrotron radiation also substantially increases the intensity of reflections from additional phases thereby increasing the sensitivity of the analysis to these phases. Identification of weak lines from additional phases is more clear when using a logarithmic scale of the intensity of reflections for the ordinate axis.

**Fig. 2.** Dependences of $RHC$ (a) and $F_n$ (b) coefficients for E110opt and E635 alloys on hydrogen content

**Fig. 3.** X-ray diffraction patterns for hydrogenated tubes made of E110opt (0 ppm — black, 320 ppm — green) (a) and E635 (0 — black, 400 ppm — green) (b) alloys obtained by transmission of 120 μm thick rings. Dots of different shapes mark the positions of the peaks:
- $\alpha$-Zr;
- $\beta$-Nb;
- Laves phase and $\delta$-hydride ZrH$_{1.66}$

**Fig. 3** clearly shows the peaks of additional phases: $\beta$-phase for E110-alloy and intermetallic phase Zr(Nb,Fe)$_2$ for E635 alloy. The observed broadening of the X-ray lines around their base and the appearance of new maxima allow us to unambiguously identify $\delta$-hydride phase (ZrH$_{1.66}$), which, as can be seen from the spectrum, is the only hydride modification in the studied samples.

### 3.3. Analysis of crystallographic texture

Based on the results of the crystallographic texture analysis for tubes made of different alloys saturated with hydrogen to different concentrations, plots of changes in the ratio of integral texture parameters $f_C/f_T$ for different hydrogen content in the product have been constructed.

According to the results shown in **Fig. 4**, the tubes made of E635 alloy have no changes in the distribution of basal axes, while in the E110 alloy there is a reorientation of basal axes from the tangential to the radial direction, i.e., the number of grains whose basal axes are oriented close to the radial direction increases. Such reorientation is possible only in the case of tensile stress acting in the tangential direction as a result of the formation of a large number of hydrides oriented circumferentially. In particular, when hydrides are formed, the material is compressed along the c-direction. Since the total volume does not change, tensile stress must be observed in the $T$- and $L$-directions. Relaxation of such stress occurs either by changing the orientation of the hydrides or by the development of twinning. For E110 alloy, as will be shown below, twinning is observed, while in E635 alloy it is suppressed.

**Fig. 5** shows the DPFs (001) for $\alpha$-zirconium and (111) for $\delta$-hydride for $L$-section based on the Debye rings obtained with synchrotron radiation.

According to the data obtained (**Fig. 5**), the texture components of $\delta$-hydride in E635 alloy tubes are the main one (001)/(110) and additional ones are (110)/(011) and (110)/(112). The hydrides with orientations (001)/(110) and (110)/(011), as well as (112) are present in approximately equal proportions in E110pt alloy tubes. The presence of hydrides with the partially axial textural component (112) (extended textural maximum is present in the region of maximum compressive stress along the radial direction) is caused by activation of twinning along the planes (1012) and (10\(\overline{1}1\)) in the $\alpha$-phase [49], in which hydrides are formed according to the established orientation relationship (0001)$_{\alpha}$ – Zr\(\{111\} \bar{\delta} – \text{ZrH}_{1.66}$.

### 4. Discussion of the results

#### 4.1. Hydride orientation change with increasing hydrogen concentration in the material

The increase in the fraction of radially oriented hydrides with increasing hydrogen content (**Fig. 2**) seems to be due to the appearance of compressive stress in
the radial direction during the formation of hydrides oriented in the tangential direction. As a consequence, tensile stresses develop in the \( T \)-direction, and, as we know, since hydride formation is associated with an increase in volume, the growth of mesoscale hydrides occurs in the direction perpendicular to the tensile stress, thereby relaxing stress. Therefore, the probability of radial hydrides increases.

The development of radial compressive stress during hydride formation in hydrogenated tubes is also indicated by a decrease in the distance between the basal planes with increasing hydrogen concentration (Fig. 4, b).

4.2. Crystallographic texture \( \alpha \)-Zr and hydride phase

Analysis of the dependences of the Kearns integral texture parameters on the hydrogen content in the alloys (Fig. 4, a) allows us to conclude that the basal axes of the grains oriented in the \( T \)- and \( L \)-directions are reoriented toward the \( R \)-direction, i.e. along the compressive stresses acting in the radial direction. This suggests that the hydride nucleation in the E110opt alloy accompanied by deformation of the zirconium matrix leads to the twinning detected in the DPF(0001) analysis (Fig. 5). At the same time, this effect is not observed in the E635 alloy, or at least is observed on a smaller scale,

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**Fig. 4.** Dependences of the \( f_R/f_T \) and \( \alpha-Zr \) lattice parameter \( c \) for middle layers of E110 (black) and E635 (red) tubes on hydrogen concentration.

**Fig. 5.** DPF(0001) (a) and \( \{111\} \) (c, d) for the \( L \)-section of a E110opt tube without hydrogen (a), as well as hydrogenated E635 (600 ppm) (c) and E110opt (700 ppm) (d) tubes; the distributions of the \( \alpha-Zr \) basal axes and \( \delta \)-hydride \( \{111\} \) axes in the \( R-T \)-section (b).
which may be due to the higher yield strength of the alloy to activate twinning preventing changes in the volume of α-matrix during hydride precipitation and twin formation.

As shown in 3.3, due to the orientation relationship performed during hydride formation as well as due to the features of their separation at the grain boundaries [9–10], the radial preferential orientation of the basal axes contributes to favorable hydride orientation in the tube and the tangential orientation contributes to unfavorable orientation. Thus, the observed grain reorientation pattern in the E110opt alloy indicates an increase in its resistance to hydride reorientation in the field of tensile tangential stresses during thermal cycles with an increase in hydrogen content.

In [40] the orientation relationships between the alpha-matrix and delta-hydride for Zircaloy-4, Zr – 1 Nb and Zr – 2.5 Nb alloys were established. The results of this work confirm the basic orientation relationship \((001)_\alpha – Zr || \{111\}_\delta – ZrH_{1.66}\) for E110opt and E635 alloys. The results of texture analysis refute the presence of the mentioned additional orientation relationship \((001)_\alpha – Zr || \{100\}_\delta – ZrH_{1.66}\) and confirm the presence of twins \((101\)\(2\)\(1\)) in E110opt alloy. This is evidenced by the presence of partially axial textural components \((110)\) α-hydride on DPF \(\{111\}\) for alloy E110opt, formed by reorientation of α–Zr basal axes at 85° and 57.2° angles for the indicated twinning systems, respectively. Thus, it can be concluded that the twinning process contributes to the appearance of a new orientation of the hydride grains due to the reorientation of the basal axes, but not because of the presence of an additional orientation relationship, but because of the release of hydrides in the twinned regions of the α-zirconium matrix.

5. Conclusions

1. The dependence of the hydride orientation coefficients on the hydrogen concentration in tubes made of Russian zirconium alloys E110 opt and E635 are obtained. It was found that an increase in the hydrogen content in the range of 40–700 wppm contributes to an increase in the number of radial hydrides in both alloys. This is due to the appearance of compressive stresses in the radial direction during the formation of tangentially oriented primary hydrides. It should be noted that the fraction of radial hydrides increases faster in the E635 alloy than in the E110 alloy. This is probably due to easier stress relaxation in the E110 alloy.

2. In the E110opt alloy, with an increase in the amount of hydrogen (hydrides), an increase in the ratio of the parameters \(f_\delta/f_\alpha\) and a decrease in the period \(c\) of the α–Zr crystal structure are observed, which indicates an increase in compressive stresses in the radial direction of the tube. Also, with an increase in the hydrogen concentration, activation of twinning along the systems \(\{101\}<101\ 1>\) and \(\{101\}<101\ 2>\) is observed, reorienting the basal axes in the direction of compressive stresses at angles of 85° and 57.2°, respectively.

3. It has been established that hydrides with the \((001)\ \{110\}\) orientation are predominantly formed in the E635 alloy, but hydrides with additional orientations \((110)<011>\) and \((110)<112>\) are also present in a smaller amount. In the E110opt alloy, hydrides with orientations \((001)<110>\) and \((110)<011>\), as well as \((112)\), are present in approximately equal proportions. The presence of hydrides with a partially axial texture component \((112)\) (an extended texture maximum is present in the region of maximum compressive stresses along the radial direction) is due to the activation of twinning along the \((101\)\(2\)\(1\))\(\{101\)\(1\)\(1\)\) planes in the α-phase, in which hydrides are formed according to with the established orientation relationship \((0001)_\alpha – Zr || \{111\}_\delta – ZrH_{1.66}\).

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