Hydrogenation and oxidation zirconium alloys
Tamás Novotny
chemistry and physics teacher MSc.

Supervisor:
Zoltán Hózer, DSc.

Doctoral School on Materials Sciences and Technologies

Hungarian Academy of Sciences
Centre for Energy Research

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Abstract

This thesis deals with the behavior of zirconium alloys under accident conditions in nuclear power plants. The author has created new devices and procedures for the charging zirconium samples with hydrogen and for determining the quantity of hydrogen absorbed by the zirconium. He has carried out experimental programs and determined the rate at which the zirconium cladding can absorb hydrogen at normal operational temperature, and also the speed at which the hydrogenated metal is oxidized in high temperature steam. By evaluating the results of mechanical tests he has determined the ductile-brittle transitional interval of zirconium cladding oxidized on one side, and also the threshold above which the hydrogenated zirconium can be considered brittle. Based on detailed tests he has determined the distribution of hydrogen in the zirconium components of those bundles that were simulating an earlier, real life malfunction.

Összefoglaló

Az értekezés az atomerőművekben használt církóniumötvözetekben üzemzavari állapotokban végbemenő változásokkal foglalkozik. A szerző új berendezéseket és eljárásokat hozott létre a církónium hidrogénnel történő feltöltésére, illetve a církóniumban elnyelt hidrogén mennyiségének meghatározására. Kísérleti programokat hajtott végre és meghatározta, hogy milyen sebességgel tud hidrogént felvenni normál üzemi hőmérsékleten a církóniumburkolat és milyen sebességgel oxidálódik a hidrogénezett fém magas hőmérsékletű gőzben. Mechanikai vizsgálatok eredményeinek kiértékelésével meghatározta az egyoldalon oxidált církóniumburkolat képlékeny-rideg átmeneti tartományát és azt a küszöbértéket, ami felett a hidrogénezett církónium ridegnek tekinthető. Részletes vizsgálatok alapján meghatározta a církóniumkompnensek hidrogéneloszlását azokban a kötegekben, amelyek egy megtörtént üzemzavart modelleztek.
I. Introduction

In nuclear reactors, zirconium alloys are widely used as cladding material for the nuclear fuel due to their low neutron capture cross section, good corrosion resistance and excellent mechanical properties (Geraszimov, 1981)\(^a\). The cladding is an important safety barrier in the reactor as it prevents the release of radioactive isotopes from the fuel.

Experiments conducted in US laboratories and research reactors in the 1960s showed that oxidized cladding became brittle far below the zirconium melting point due to steam oxidation (Parker, 1965; Hobson, 1973; OECD, 2009)\(^b,c,d\). During the oxidation, important microstructural changes occurred in the cladding (Hache, 2000)\(^e\). It was also demonstrated that burnup effects on embrittlement are largely due to hydrogen that is absorbed in the cladding during normal operation. (Billone et al., 2008)\(^f\).

In Hungary the experimental investigation of the zirconium cladding used in nuclear power plants began in the 1990s in the MTA KFKI AEKI, the predecessor of the MTA EK. The first studies compared the Russian and Western alloys (Maróti, 1997)\(^g\). The parameters that were required for computer codes to predict the changes in the Russian alloy were determined. The effects of irradiation, oxidation and interactions between the different materials in the active core were investigated in small-scale experiments (Hózer, 2008)\(^h\). In integral experiments, several incidents and accidents were modeled with electrically heated fuel bundles in the CODEX facility (Hózer et al., 2003; Hózer et al., 2006)\(^i,j\).

When I started working at AEKI in 2006, I joined the zirconium experimental research. At that time, several questions were raised on what extent and which factors influence the embrittlement of fuel cladding. It turned out that more detailed examination was necessary on the samples come from the integral experiments. Foreign research (Billone et al., 2008)\(^f\) pointed out that the load-bearing capacity of oxidized zirconium is significantly influenced by the hydrogen concentration of the metal before the incident. The Russian fuel company improved the E110 alloy containing 1% niobium used in the Paks Nuclear Power Plant. The first measurements showed that the new E110G had much better load-bearing capabilities in oxidized state and did not pick up as much hydrogen as the traditional alloy did (Yegorova et al., 2005; Salatov, 2009; Niklulin et al., 2011)\(^k,l,m\). For further research on Russian alloys new methods and equipment were required for charging zirconium samples with hydrogen and for analyzing oxidized and hydrogenated samples. In this dissertation, I report these results.
II. Objectives

During my work I designed new equipment and series of experiments with the general purpose was to conduct detailed examinations in order to produce information and data of zirconium claddings – used in the Paks Nuclear Power Plant –, which would contribute to the safe and economical operation of the nuclear power plant. In the experiments those simulation of malfunction situations are emphasized which might lead to processes that challenge the integrity of the fuel.

At the beginning of the research programs presented in my dissertation, we set up the following goals with my colleagues:

1) A measurement procedure and experimental device had to be created to determine the amount of hydrogen absorbed by zirconium samples during various oxidation and corrosion processes. Hydrogen content has significant effect on metal ductility, so knowing this value is very important to evaluate oxidation measurements.

2) A new test equipment was needed to be designed and constructed for filling hydrogen into zirconium specimens. The device can be used to model hydrogen uptake during pre-accident processes (normal reactor operation).

3) It was necessary to investigate what degree of hydrogen uptake of the zirconium alloys leads to embrittlement. This is an important information to interpret the embrittlement in the oxidation process with hydrogen uptake.

4) In addition to earlier series of measurements, it was necessary to examine the effect of the initial hydrogen content on the high temperature steam oxidation of the zirconium claddings and on the embrittlement of the oxidized samples.

5) As a continuation of earlier two sided oxidation experiments, a new measurement program had to be designed and performed in which only the outer surface of the cladding was oxidized. The purpose of the series of experiments was to determine the ductile-brittle transition of oxidized zirconium in case of one sided oxidation.

6) In 2003 during the incident of Paks NPP the fuel suffered brittle damage in the cleaning tank. Direct examination of the fuel claddings was not possible. Therefore, it was very important to map the amount and spatial distribution of absorbed hydrogen in the zirconium components of the fuel bundles using the integral experiments carried out in the CODEX facility. The measured data can refine the concept of the incident history.
III. Test methods

Gas system for hydrogen filling of zirconium alloys

For the hydrogenation of the E110G and E110 alloys, I connected a three-zone tube furnace used for high temperature oxidation to a gas inlet system and a vacuum system. The change of the pressure was continuously registered during hydrogenation. The decreasing pressure indicated that the zirconium absorbed hydrogen. When the hydrogen uptake of the samples was completed, the pressure drop practically discontinued. Then the sample holder was pulled back into the cold part of the quartz tube. The amount of absorbed hydrogen was checked by mass measurement and hot extraction method.

Oxidation equipment

The high temperature steam oxidations were carried out in an experimental apparatus consisting of a steam generator, a three-zone resistance furnace, a temperature control system and a steam condenser. The samples (E110G and E110) were oxidized at 1000 °C and 1200 °C under flowing steam:argon (88:12 vol%) and under isothermal conditions. At the end of the oxidation, the samples were moved to the cold part of the quartz tube.

Determination of hydrogen content by hot extraction method

After desorption at high temperature the amount of absorbed hydrogen in the cladding samples was determined by the thermal conductivity detector (TCD) of CHROMPACK 438A gas chromatograph. The sample weighed on an analytical balance was placed on a quartz boat and was put into furnace previously heated to stable, 1150 °C temperature. At this temperature, all the hydrogen is released from the sample, which directly gets into the gas chromatograph by the carrier gas and passed through the charged column into a thermal conductivity detector (TCD). During the measurement, the TCD signal voltage proportional to the hydrogen concentration was continuously recorded. During the evaluation, the area of the TCD sign above the baseline was integrated and compared with the integral of the calibration curve. This gives the amount of hydrogen released from the sample with known mass.

Ring compression tests

Radial ring compression tests of E110G and E110 samples were conducted at room temperature using INSTRON 1195 universal tensile test machine. Force-displacement curves were recorded. Their evaluation was based on the shape of the curves and the specific failure energy.
IV. New scientific results, thesis points

1. I developed a hot extraction method that can measure the hydrogen content of oxidized zirconium alloys. [1][2]

   With this new method it possible to measure the hydrogen content of zirconium alloys relatively quickly and easily. Above 1100 °C, the absorbed hydrogen is released from the sample, which can be measured by the thermal conductivity detector. From the hydrogen content of the sample it can be concluded whether the oxidized zirconium shows ductile or brittle behavior.

2. I developed a new technology for hydrogenation of zirconium alloys. [1]

   I built a gas system with gas inlets and pressure gauge in which the hydrogen can be absorbed by the zirconium alloy under controlled conditions. In the apparatus I hydrogenated E110G and E110 alloys to a predetermined hydrogen content.

3. Based on the ring compression tests of unoxidized, hydrogenated Zr samples, I found that the samples are brittle above 3000 ppm. [1][3][4]

   I hydrogenated E110G and E110 alloys under controlled conditions and I found that the claddings lose their ductility above 3000 ppm hydrogen content and become brittle. This barrier can be used to determine the ductile to brittle transition of the fuel claddings.

   I concluded that the normal hydrogen uptake of the fuel cladding has a negative effect on its mechanical properties at the occurrence of a LOCA event.

4. I performed oxidation experiments with hydrogenated E110 and E110G claddings. [1][4]

   I examined the effect of the normal operational hydrogen uptake of the fuel cladding at the nuclear power plant on the behavior of the cladding under LOCA conditions. I made high temperature oxidation experiments in steam with the previously hydrogenated E110G and E110 samples.

   I found that there is no significant difference in the oxidation kinetics of the same type of alloys with different hydrogen contents.
5. Based on the function of the oxidation time and temperature, I have determined the range where the E110 retains its ductility in case of one-side-oxidation. [5]

I compared the results of the one-side-oxidation with the results of previous double sided oxidation tests performed at the institute. I found that the two-sided oxidation tests give more conservative results than the one-sided oxidation measurements, as in case of one-sided oxidation the embrittlement of the cladding material occurs after much longer time than it would be expected from the double side oxidation measurements. This is very advantageous from reactor safety perspective, as brittle fracture of the fuel cladding is not expected under any circumstances as long as the ductile state is maintained.

6. I measured the axial hydrogen distribution of zirconium alloys in experimental samples considered representative for the 2003 Paks incident. [3][6]

The integral tests performed with CODEX unit were successfully modeled the 2003 Paks cleaning tank incident. My measurement data clarified the assumptions of the conduct of the incident. The data suggested that in case of low oxidation rate the hydrogen uptake of the metal alloy was proportional to the degree of oxidation. But in the case of high oxidation rate, the amount of remaining metal limited the hydrogen uptake. The measurements provided data to validate and develop the computer codes used for the prediction of behavior of fuel rods in accident situations.
V. Utilization possibilities of the results

Utilization of the results, described in Thesis 1

The developed method for measuring the hydrogen content of zirconium alloys provided a new opportunity to establish the oxidation embrittlement criteria. The hydrogen uptake data determined by the process have been included in numerous projects and publications [3][6].

Utilization of the results, described in Thesis 2

The production of hydrogenated samples allows the revision of the criteria for the maximum oxidation of the fuel cladding. Irradiation of some of the samples I hydrogenated has begun in the Budapest Research Reactor to evaluate the combined effect of irradiation and hydrogen uptake on changes in cladding characteristics.

Utilization of the results, described in Thesis 3

The maximum allowed hydrogen content specified by the fuel manufacturer is 400 ppm in the zirconium cladding. This was confirmed by my measurements that up to 400 ppm the E110 and E110G zirconium fuel cladding is really ductile.

Utilization of the results, described in Thesis 4

The unique oxidation measurement results of hydrogenated samples allow the development of new oxidation kinetic models.

Utilization of the results, described in Thesis 5

Measurements have proved that a less conservative approach is sufficient in case of one-sided oxidation than a double-sided oxidation process, because the embrittlement occurs after much longer time.

Utilization of the results, described in Thesis 6

My measurements of the hydrogen contents can be assigned to the data obtained in large-scale experiments (CODEX), to determine the degree of oxidation and hydrogen content where the fuel become brittle. My measurements provided additional new data to develop and validate the fuel behavior simulation codes in accident situations.
VI. References


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VII. Scientific publications of the candidate related to PhD theses


VIII. Further scientific publications of the candidate


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