High temperature oxidation of zirconium alloys used in nuclear power plants

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I. Background

The main user of zirconium-based alloys is the nuclear industry, where they are applied as fuel claddings and structural elements of fuel-assemblies (Brown et al., 2005). The fuel cladding plays an important role in preventing the release of fission products from a nuclear power plant into the environment, under both normal and accident conditions. Zirconium alloys developed for fuel claddings have excellent corrosion resistance and very good mechanical properties under normal operating conditions. However, high temperature and corrosive atmospheres (e.g. steam, steam-hydrogen, air, steam-nitrogen) can evolve under incident and accident situations, which can lead to the rapid oxidation of the cladding. The oxidation can cause the mechanical deterioration of the cladding and in extreme cases even the loss of cladding integrity.

The oxidation of the cladding takes place in pure steam atmosphere during Loss of Coolant Accident (LOCA). The zirconium-steam reaction results in the formation of an oxide layer on the outer surface of the cladding. The oxidation is accompanied by intensive hydrogen production. The formed hydrogen is partly absorbed by the zirconium (Frecska et al., 1995), which contributes to the embrittlement of the cladding. In certain situations, a hydrogen-rich steam atmosphere can evolve in the vicinity of the fuel cladding (e.g. cleaning tank incident of the Paks nuclear power plant Unit 2). In this case, the cladding can absorb large amounts of hydrogen from the gaseous environment (Hózer et al., 2003). In the event of a loss of coolant incident of the spent fuel storage pool or a reactor vessel failure due to a severe accident, the oxidation of the cladding can occur in air or steam-air mixture. Not very likely, but the fuel cladding may interact with nitrogen or nitrogen-containing steam due to the failure of the hydroaccumulators (Kostka, 2018; Nagy, 2018).

In order to operate nuclear power plants safely, it is necessary to thoroughly learn about and map the above-mentioned processes. Several experiments have already been carried out worldwide on the oxidation of zirconium alloys. This type of research was also performed at the Atomic Energy Research Institute (AEKI) of the Hungarian Academy of Sciences (Frecska et al., 1995; Frecska et al., 1997; Matus, 2000). In the meantime, new zirconium alloys have emerged and the methods used for their tests have also improved, which has justified the implementation of new series of experiments.

My PhD dissertation was based on my scientific research work (from 2004 to the present) in the Fuel and Reactor Materials Department of the Centre for Energy Research.
II. Objectives

The main direction of my research was to study the high temperature oxidation of E110 and E110G type zirconium fuel claddings.

I aimed to explore the effect of oxidation conditions on the oxidation kinetics of E110 and E110G alloys, the quality of the oxide layer formed on the surface and, in some cases, the amount of hydrogen taken up by the cladding. In the course of my research, I focused on the examination of the effect of atmospheres potentially formed in incident and accident conditions. Therefore, I planned to perform the experiments in steam, hydrogen-rich steam, and nitrogen-containing atmospheres (air, air-steam mixture, nitrogen, nitrogen-steam mixture). My goal was also to compare the high temperature oxidation behavior of the two alloys.

Since the oxidation associated with the cracking of the oxide layer is considered to be one of the main problems of a possible LOCA event, I paid special attention to the study and monitoring of the breakaway oxidation with oxide layer cracking. In addition, I was looking for an answer to the question of in which temperature range the studied fuel claddings are susceptible to this type of oxidation. It was also one of my goals to create a so-called ‘breakaway oxidation map’ of the E110 cladding. In order to achieve this, I sought to develop a method that can quickly and unambiguously determine when the oxide layer cracks at different temperatures.

III. Test methods

High temperature oxidation tests

A high temperature tube furnace with a quartz tube was used for the oxidation experiments. The experimental apparatus consisted of a steam generator, gas system (for argon, hydrogen, nitrogen and air supply), a horizontally arranged three-zone resistance furnace and a condensing system. The furnace can optionally be coupled to a thermal conductivity detector (TCD), which makes it possible to continuously monitor the hydrogen content of the gas mixture (carrier gas and hydrogen formed) flowing out of the tube furnace.

The tests were performed in different oxidizing atmospheres in the temperature range of 600 °C to 1200 °C under isothermal conditions. After stabilization of the temperature and gas flow, the quartz boat with the sample was pushed into the heated zone of the furnace. At the end of oxidation, the sample was withdrawn to the cold part of the equipment. During the experiments, both the outer and inner surfaces of the specimens were oxidized. The changes
during the chemical reactions (mainly the extent of oxidation) were characterized by the measured mass gain.

**Post-test examinations**

Optical microscopy (OM), scanning and transmission electron microscopy (SEM and TEM), and energy dispersive X-ray microanalysis (EDX) were applied for morphological studies and elemental analysis of some selected samples.

Samples embedded in the epoxy resin were etched with 0.5% hydrogen fluoride after mechanical polishing to reveal the grain structure of the material. Metallographic examination of cross sections was performed with a Reichert Me-F2 optical microscope.

The prepared samples were made conductive by applying a thin layer of evaporated carbon. For the morphological analysis of the samples oxidized in steam, a JEOL Superprobe 733 type electron beam microanalyzer was used in backscattered electron (BEI) mode. In some cases, electron microscopy was performed directly without resin embedding with a Philips SEM 505 scanning electron microscope. Secondary electron (SEI) images were taken of the directly examined samples.

A LEO 1540XB scanning electron microscope equipped with a Gallium focused ion beam (Ga FIB) was used for microscopic examination of the samples oxidized in the steam - nitrogen mixture. With this equipment, sections with a depth of a few micrometers were prepared to investigate the depth distribution of nitrogen and oxygen. A Themis 200 spherical aberration corrected transmission electron microscope from Thermo Scientific was used to determine the individual crystal sizes of nitrides and oxides.

Energy dispersive electron beam microanalysis (EDX) was performed with a RÖNTEC thin-window analyzer and an Oxford X-Mac-20 analyzer attached to a Thermo Scientific Scios2 Dual Beam microscope.

**Determination of hydrogen content**

The amount of hydrogen absorbed by the oxidized zirconium samples was determined using a thermal conductivity detector after high-temperature desorption (so-called hot extraction). Desorption was performed in a tube furnace with a quartz tube at 1150 °C.

In some cases, the amount of absorbed hydrogen was quantified with an ELTRA, ELEMENTRAC® OH-p type oxygen-hydrogen elemental analyzer.
IV. New scientific results

1. I developed an online measurement method for the investigation of the breakaway oxidation with oxide layer cracks under isothermal conditions. I demonstrated with experiments that the continuous detection of hydrogen released during high-temperature steam oxidation of zirconium alloys can be applied for monitoring breakaway oxidation. With this method, it is possible to determine quickly and clearly when the oxide layer cracks at a given temperature, leading to an acceleration of the oxidation of the fuel cladding. Despite the complexity of the breakaway process, the measurement can be well reproduced with this method [1].

2. I prepared the so-called “breakaway oxidation map” of the E110 type nuclear fuel cladding and determined the temperature range (900 – 1050 °C) where the breakaway oxidation of the E110 cladding takes place in a short time (300 – 500 s). Using the developed online method, I proved that the E110G cladding does not show breakaway oxidation when oxidized in steam in the examined temperature range (800 – 1200 °C) [1][2][3].

3. I found that the presence of hydrogen in the steam atmosphere does not accelerate the high temperature oxidation kinetics of E110 and E110G alloys. I proved by experiments that in the studied range (900 – 1100 °C, ≤65% hydrogen content) the steam oxidation of E110 alloy is slowed down by the hydrogen-rich atmosphere and there is no detectable effect on the oxidation of E110G [4][5].

4. I found that the hydrogen absorption of the E110 cladding is much more intense in hydrogen-rich steam than in pure steam atmosphere. I have shown by measurements that the hydrogen content of the E110 cladding oxidized in hydrogen-rich steam can be up to several times the hydrogen content of the cladding oxidized to the same extent in pure steam [4].

5. I proved by experiments that in steam with higher air content (50%) and in pure air atmosphere, the oxidation of E110 and E110G alloys is faster at the studied temperatures than in steam without air. The effect of the air-containing oxidizing medium is more significant on the E110 alloy. With detailed measurements, I created a database for both alloys, which characterizes the kinetics of air oxidation at 10, 50 and 100% air content [6].

6. Based on oxidation experiments in nitrogen-containing steam, I found that the presence of nitrogen accelerates the weight gain of E110 and E110G alloys compared to pure steam oxidation under certain conditions, and I pointed out the different behavior of the alloys. I
found that the E110G alloy behaved similarly or more favorably than the E110 alloy at the studied temperatures (except 1200 °C). I also found that breakaway oxidation can also occur in E110G alloy in steam with high nitrogen content (50%) [7][8].

V. Utilization possibilities of the results

In order to maintain the safety of nuclear power plants, it is essential to study and to get to know as thoroughly as possible the processes and phenomena that take place in the fuel claddings under incident and accident conditions. Research results on high-temperature oxidation and hydrogen uptake of E110 and E110G claddings can be used for computer modeling of fuel behavior processes.

Based on experiments with the E110G cladding, new oxidation correlations were developed in the MTA EK to describe the steam oxidation of E110G, which were implemented into the FRAPTRAN and TRANSURANUS codes used for safety analyses (Kozsda-Barsy, 2016). At the same time, the oxidation correlation applied to the E110 cladding was also refined for oxidation outside the breakaway range (Király, 2014).

The results obtained from experiments in pure steam may contribute to the support of the new LOCA criteria [22].

The results of the experiments performed in hydrogen-rich steam facilitated the understanding of the processes that took place in a cleaning tank incident at the Paks nuclear power plant Unit 2 [5].

A large number of experiments performed in a nitrogen-containing oxidizing medium provide new, more detailed data for kinetic modeling of severe accident conditions at a nuclear power plant. Most of the severe accident codes do not have currently a model that simulates the zirconium-nitrogen reaction, which shows how important these results are. Microstructural examination of oxidized specimens contributes to the detailed characterization of material structures formed during a severe accident.
VI. References


VII. Scientific publications related to theses


IF:1,313


VIII. Further scientific publications


