THE PROPERTIES OF NUCLEAR FUEL CLADDING MATERIALS UNDER NORMAL OPERATION AND ACCIDENT CONDITIONS

THESES OF PHD DISSERTATION

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1. INTRODUCTION

In the core of most nuclear reactors, enriched uranium dioxide fuel tablets are housed in zirconium alloy tubes surrounded by high-temperature and high-pressure water. Fuel load is further increased by increasing reactor performance at many nuclear power plants, including the Paks Nuclear Power Plant, lengthening fuel campaigns, and increasing fuel specific energy gain through increased burnout.

Instead of the zirconium-niobium cladding E110, which is currently used in Russian VVER-type pressurized water reactors and has been relatively well-known in recent decades, the Russian fuel manufacturer has in recent years developed a new version which is already used in several power plants and is expected to be introduced in Hungary as well.

In case of changes in operation and the introduction of newer fuel types, it must be demonstrated that the new fuel elements can withstand the expected loads under both normal and off-normal conditions. The design and licensing of new third generation power plants will also require demonstration of fuel compliance. One of the key questions in safety analyzes is whether the zirconium cladding of the fuel - as an important engineering barrier - remains intact, as damage to the cladding and loss of integrity can lead to the escape of radioactive isotopes. The introduction of new cladding materials requires verification of compliance with the criteria developed for the previous cladding, as well as verification of the numerical models used to model processes in the cladding and describe changes in the cladding material and, if necessary, their modification. The development and validation of the computer code models used for the calculations require measurement data that is representative of the various states of the fuel elements and provides information on the processes that take place in the fuel element.

In addition to the information supplied by the fuel manufacturer, it is very useful to for both licensing and operation to have independent measurements and modeling experience in the country where the fuel is used. In Hungary, the researchers at the Hungarian Academy of Sciences Centre for Energy Research (MTA EK) and its predecessor (AEKI) have been engaged in the experimental investigation of zirconium claddings for more than twenty years, as well as in the modeling of processes that occur during normal operational in accident scenarios. During my PhD research I joined the Laboratory of Fuel and Reactor Materials of the MTA EK and did experimental and modeling work. In my PhD dissertation I report on the results of this, relying heavily on research publications published with my active participation.

2. OVERVIEW OF THE FIELD OF RESEARCH

The zirconium alloy claddings of the fuels used in pressurized water reactors are corroded during normal operation. Both the oxides and the hydrogen formed in the oxidation reaction can be dissolved in the metal. In nuclear power plants, in case of a loss of coolant, the fuel elements may become heated to high temperatures and may intensively oxidize. The high temperature heat treatment itself changes the structure of the cladding material, especially when the temperature reaches the phase transition temperature range (850-900 °C depending on the alloy), above which the crystalline structure of the zirconium is transformed. Oxygen and hydrogen dissolved in the metal initiate changes in the material of the cladding which cause the plasticity of the metal to diminish and – above a certain concentration – the cladding may fail in a brittle way due to mechanical stresses.

Stationary and transient computer code simulations of the fuel behavior can predict the behavior of the claddings in normal operation and in case of accidents. The codes include the measured and calculated material properties of the cladding materials and the correlations related to their behavior in different conditions (high temperature, oxidation in different atmospheres, high internal pressure). These data must be provided for each material in order to carry out the safety analyzes.

The mechanical properties of the newly introduced cladding alloys must be confirmed by tensile tests and oxidation tests. Identifying key mechanical properties (such as tensile strength, yield strength, creep) and sensitivity to chemical and thermal treatments is essential for the safety analyzes. It is also important to quantify the effect of hydrogen uptake on embrittlement in operational and accident conditions.

Based on the measured results obtained from simulations of normal operation conditions and high temperature oxidation, new oxidation kinetic models can be constructed. The conservative Baker-Just correlation and the best-estimate Cathcart-Pawel oxidation models are used worldwide to describe the oxidation of zirconium cladding alloys in high-temperature steam. However, these models have been adapted based on measurements with tin-containing zirconium alloys (such as Zircaloy-4), which are common in Western nuclear power plants, and are not suitable for describing the oxidation of significantly different materials, such as the zirconium-niobium alloy E110.

Over the past two decades, fuel manufacturers have begun intensive development to meet market needs and have developed, approved and introduced several new cladding alloys (such as ZIRLO™, M5™) with improved properties. The number of measurements available in the literature on the mechanical and oxidation properties of the newly developed zirconium-niobium cladding alloy E110G (produced by a different technology) – soon to be introduced by the Russian fuel manufacturer – is very limited. A large amount of measured data is required to establish the safety analyzes and to describe the behavior of the cladding alloy under various conditions. To this end, a series of measurements with the new cladding alloy have been launched at the Hungarian Academy of Sciences and around the world.

3. ANTECEDENT

The high-temperature oxidation properties of the newly developed Russian cladding material E110G differed from those of the E110 and Zircaloy alloys to the extent that new code-additions and new best-estimate and conservative oxidation correlations were required. Between 2010 and 2012, several high temperature oxidation tests were performed in AEKI / MTA EK with both E110 and E110G claddings at temperatures between 600 °C and 1200 °C, oxidizing ring samples in an atmosphere containing argon and steam.

Based on the results of mechanical tests with oxidized rings, the hardening and embrittlement of the E110G cladding samples after oxidation in high temperature steam was significantly lower than the rapid embrittlement of the E110 alloy. The room temperature ring compression tests showed that at the same oxidation temperature, the E110G alloy could be oxidized five times longer to reach the ductile - brittle transition than the E110 alloy.

The results showed that at 800 °C and 1100 °C the oxidation of E110G was slightly faster than that of E110, but the difference was not significant, whereas at 900 °C and 1000 °C the oxidation of the E110 alloy was much more intense. The oxidation of E110G does not accelerate, there is no indication of oxide layer spalling (breakaway) in the tested temperature range.

Since 1998, tensile tests have been carried out at AEKI to measure the circumferential (tangential) tensile strength of the fuel claddings. Initially, machined ring specimens with two narrowed gauge regions were used, this was later changed to 2 mm wide whole rings cut from the tubes. Ring compression and four-point bending were used to test the plasticity of the tubes.

The strength-modifying effect of some chemical treatments simulating normal operational corrosion and accident behavior has long been studied, but the effect of the temperature of these pre-treatments (e.g. oxidation, hydrogenation) has not been analyzed so far. The effects of this heat treatment could be deduced from only a few measurements.

4. RESEARCH GOALS

During the planning of the PhD research activity presented in the dissertation, I researched and compared the mechanical and chemical properties of the currently used and the newly developed cladding materials. These projects were initiated to support the operation of Paks NPP, primarily to provide detailed data on the behavior of zirconium alloys used in a nuclear power plants under various conditions. The following aspects justify the initiation of the research:

I. Domestic and foreign experiments showed significant differences between the oxidation in high temperature steam of the of conventional E110 alloy made from iodide and electrolytic zirconium and the E110G alloy made from sponge zirconium from the Kroll process. In the computer models (e.g. FRAPTRAN code) the oxidation kinetic correlations used for the E110 alloy were not adequate for the E110G alloy. Therefore, based on existing data and additional measurements from the experimental design, new correlations were needed to be established to describe the oxidation of E110G in high temperature steam.

II. The tensile strength of the cladding is a very important input parameter for safety analyzes. The material structure properties of drawn pipes, such as the fuel claddings, have significant anisotropy. Therefore, in order to measure axial and tangential tensile strength separately, the optimal specimen geometries and the measuring conditions were to be determined. In order to prepare the specimens from the cladding tubes, the effects of the different machining technologies needed to be studied.

III. Axial and tangential tensile tests performed on untreated specimens can determine the tensile strength of the as-received material. In addition to room temperature measurements, high temperature tests should also be included to cover the normal reactor operating parameters.

IV. It was previously known that zirconium could absorb hydrogen during normal operation due to corrosion processes and radiolysis, but no specific data were available on how this would alter the tensile strength of E110 and E110G alloys. Therefore, measurements were needed to derive the tensile strength of slightly hydrogenated alloys, close to power plant conditions, as a function of hydrogen content and temperature.

V. In the case of off-normal conditions, important structural changes can occur in the zirconium cladding if the temperature reaches the phase transition range. Inert gas heat treatments and tensile tests were necessary to evaluate the effect of these changes at different temperatures on the E110 and E110G alloys as a function of the heat treatment time.

VI. During design basis accidents the zirconium cladding may be slightly oxidized, which may alter the load bearing capacity of the alloy. This can have important consequences when moving the fuel elements after an incident. In order to determine the tensile strength characteristic of the oxidized claddings, mechanical tests with slightly pre-oxidized samples had to be planned, performed and evaluated.

5. THE RESEARCH PROGRAM

While working in the Fuel and Reactor Materials Department of the Hungarian Academy of Sciences Centre for Energy Research, I designed experimental programs, developed models and performed evaluations that were well suited to the projects of the research institute. The research was supported by MVM Paks Nuclear Power Plant, and the National Research, Development and Innovation Office (NKFIH) in the framework of the Zirconium Materials Science Research project.

Significant differences were found between the two alloys in earlier high temperature oxidation experiments despite their very similar composition. In order to further improve the FRAPTRAN code and to verify existing models, I performed post-test calculations of the oxidation experiments performed in high temperature steam with the new E110G cladding. Based on the data, a new oxidation kinetics was established and supported by further experiments. The resulting best-estimate oxidation kinetics was included in the FRAPTRAN code and later in the TRANSURANUS code.

Based on the available literature and our own experimental data, I determined and compared the mechanical properties of the currently used E110 alloy and the new E110G alloy tubes of a different production technology. In addition to the analysis of the untreated, as-received samples, the effect of treatments (inert heat treatment, oxidation in steam, hydrogenation) on the tensile strength was also investigated.

Mechanical tests have been performed to determine the axial and tangential tensile strength of as-received and pre-treated claddings. In developing the new geometry of the specimens to be used for the tensile tests, I relied on the results of research carried out abroad and the data available on the topic in the domestic and foreign literature. In order to gain a deeper understanding of the processes involved in the measurements and to support the planned experiments, the sample geometries selected for tensile tests were also modeled by my colleagues using finite element method and the results of the tensile test simulations were evaluated.

Axial and ring tensile tests were performed with untreated, oxidized, hydrogenated and heat-treated specimens made from the fuel cladding tubes at room temperature, elevated temperature (150 °C) and near the operating temperature (300 °C). The experimental design included slight oxidation and hydrogen uptake resembling normal operating conditions. The axial and ring specimens were exposed to oxidation in steam or heat treatment under the same conditions in inert atmosphere, and in some cases they absorbed a few hundred ppm of hydrogen. To test the effects of the heat treatment and the oxidation separately, and to refine the oxidation kinetics, ring specimens were treated at various temperatures and times. Mechanical tests were performed on both the new E110G and the currently used E110 alloys and their axial and tangential tensile strength was determined and compared. I evaluated the effects of the above treatments on the tensile strength of the cladding alloys.

6. NEW SCIENTIFIC CONTRIBUTION TO KNOWLEDGE

Thesis 1: Based on the available data and the new data measured based on my experimental design, I have designed and validated a best-estimate and a realistically conservative reaction kinetic correlation, which describes the oxidation of the E110G alloy in high temperature steam with high accuracy. Within the new correlation I divided the oxidation into three ranges between 600 °C and 1200 °C. In addition, I introduced the dependence on the total oxidation time and, instead of the prevalent kinetic description using the square root of the oxidation time, I approximated the measurement data with new functions and different power law equations. With these changes the new correlations approximate the measured values with higher accuracy than the previous correlations [P1, P4].

Thesis 2: I have investigated the methodology of the direction-dependent measurement of the tensile strength of the nuclear fuel claddings. I designed a series of experiments to measure the axial and tangential tensile strength of the cladding tubes separately. Based on descriptions found in the literature, I examined several test specimen geometries and three types of manufacturing technologies. The axial tensile test specimen I designed is a 50 mm long full tube with two parallel weakened tear regions, and two drilled holes for clamping. For the measurement of the tangential tensile strength, I chose 2 mm wide cladding rings from among several possible geometries [P2].

Thesis 3: I designed a series of measurements to compare the mechanical properties of E110 and E110G zirconium alloy cladding tubes and to evaluate the effects of chemical and thermal treatments modeling normal operation and accident conditions. The tensile strength of untreated E110 and E110G cladding tubes was determined at room temperature and at high temperature, measured separately in axial and tangential directions. According to my measurements, the room temperature axial tensile strength of E110G samples was 11% higher than that of E110 samples, but at 300 °C this difference became insignificant. The circumferential tensile strength for both alloys and at all three temperatures was approximately 12% lower than the axial tensile strength [P2, P3, P5, P6].

Thesis 4: The effect of the inert heat treatment (at different temperatures and treatment times) on the tensile strength of E110 and E110G alloys was determined. The measured tensile strength of the two alloys changed differently as a result of the heat treatments. The heat treatment at 600 °C reduced the tensile strength of both alloys, however, higher temperature treatments, especially at 900 °C, increased the tensile strength. The duration of the heat treatment had no significant effect on the tensile strength [P3, P5, P6].

Thesis 5: By means of measurements I separated the effects of oxidation in high temperature steam – that can occur in design basis accident conditions (1-5 ECR%) – from the effects of the similar inert heat treatment. While the heat treatment increased the tensile strength, the oxidation itself reduced the tensile strength of E110 and E110G alloys by 5-10% [P3, P5, P6].

Thesis 6: I determined that the hydrogen uptake of 400 ppm, that is allowed by the fuel manufacturer to occur during normal operation, does not affect the tensile strength of E110 and E110G cladding alloys at room temperature and at 300 °C [P3, P5, P6].

7. SCIENTIFIC PUBLICATIONS SUPPORTING THE THESES

[P1]: Márton Király, Katalin Kulacsy, Zoltán Hózer, Erzsébet Perez-Feró, Tamás Novotny: High-temperature steam oxidation kinetics of the E110G cladding alloy. Journal of Nuclear Materials 475 (2016) 27-36

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[P2]: Márton Király, Dániel Mihály Antók, Lászlóné Horváth, Zoltán Hózer: Evaluation of axial and tangential ultimate tensile strength of zirconium cladding tubes. Nuclear Engineering and Technology 50 (2018) 425-431

https://www.sciencedirect.com/science/article/pii/S1738573317307003

[P3]: Márton Király, Zoltán Hózer, Lászlóné Horváth, Tamás Novotny, Erzsébet Perez-Feró, Nóra Vér: Impact of thermal and chemical treatment on the mechanical properties of E110 and E110G cladding tubes. Nuclear Engineering and Technology, Volume 51, Issue 2 (2019) 518-525

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[P4]: M. Király, K. Kulacsy, E. Perez-Feró: High-temperature steam oxidation kinetics of the new E110G cladding alloy. Proceedings of XXI. QUENCH Workshop, 27-29. October 2015, Karlsruhe, Germany, p. 46-49

[P5]: M. Király, Z. Hózer, D. M. Antók, M. Horváth, I. Nagy, R. Nagy, T. Novotny, E. Perez-Feró, N. Vér: Overview of the experiments performed with Russian claddings at MTA EK. Top Fuel 2016 Light Water Reactor Fuel Performance Meeting, September 11-15. 2016, Boise, ID, USA, Volume I., p. 41-49

[P6]: M. Király, Z. Hózer, D. M. Antók, M. Horváth, I. Nagy, R. Nagy, T. Novotny, E. Perez-Feró, N. Vér: Overview of the experiments performed with Russian claddings at MTA EK. 12th International conference on WWER fuel performance, modelling and experimental support, 16-23. September 2017, Nessebar, Bulgaria, p. 221-228.

8. LIST OF OTHER SCIENTIFIC PUBLICATIONS

R. Nagy, M. Király, T. Szepesi, A. G. Nagy, A. Almási: Optical observation of the ballooning and burst of E110 and E110G cladding tubes. Nuclear Engineering and Design, Volume 339 (2018) p. 194-201

R. Nagy, M. Király, T. Szepesi, A. G. Nagy, A. Almási: Optical measurement of the high temperature ballooning of nuclear fuel claddings. Review of Scientific Instruments, Volume 89, Issue 12 (2018) Paper 125114

R. Nagy, M. Király, D. M. Antók, L. Tatár, Z. Hózer: Dynamic finite element analysis of segmented mandrel tests of hydrogenated E110 fuel cladding tubes. Materials Today Communications, Volume 24 (2020) Paper 101005