Behaviour of oxide layer on Zircaloy cladding tube under steam starvation conditions. Tests at temperatures between 1250°C and 1450 °C

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Introduction

Results of the tests on long-duration annealing of pre-oxidized Zircaloy cladding tubes in the inert atmosphere with an annealing temperature of 1250 °C are presented. The objective of the tests was the investigation of the reduction kinetics of the oxide layer during a steam starvation phase by the progression of core drying during a severe accident. The homogeneous formation of the α-Zr(O) precipitations inside of the oxide layer and formation of the α-Zr(O) scale on the cladding outer surface were detected in addition to the oxide layer thickness change. The phenomenon should have a strong influence on hydrogen release during the following quench phase.

1. Motivation and Objectives

Steam starvation conditions on fuel rod surfaces are possible during a severe accident due to dry-out of the reactor core and blockage formation. The oxide layer of the cladding tube surface will be reduced under these conditions. Therefore the knowledge about the oxide layer reduction processes is important for severe accident management measures. Up to now detailed investigations were only performed for the description of the oxide layer *growth* during cladding oxidation at isothermal conditions [1] and non-isothermal conditions [2].

The oxide layer *reduction* processes under non-isothermal conditions were investigated at FZK during the last two years, only in the temperature region between 1400°C and 1490°C (temperature drift during the test between these values) [3, 4]. These tests on degradation of oxide layer during annealing in argon atmosphere unexpectedly show the formation of α-Zr(O) *precipitates*, homogeneously distributed inside of the oxide layer. The work presented describes the results of the new FZK experiments, which were performed at significantly lower temperature (1250…1350 °C) and showed nevertheless the bulk precipitate formation as well as the development of the *metallic scale* on the outer surface of the oxide layer during annealing. Furthermore results of two new tests under isothermal conditions at 1400 °C are presented, which also demonstrate the development of both bulk metallic precipitates and outer metallic scale.

2. Applied Tools

Six empty Zry-4 sealed tubes with a length of 15 cm were pre-oxidized and afterwards annealed in the IMF QUENCH rig [5]. Two temperature sensors were applied: (a) a pyrometer to control the HF-generator and (b) an internal TC to reliably measure the temperature of the sample under thermodynamic-balance conditions. The samples were pre-oxidised in an argon (90 l/h)–steam (100 g/h) mixture flow at ~1250 °C to reach the two target initial oxide layer thicknesses of 180 and 240 µm. In the next stage the pre-oxidised samples were annealed for 40, 90 and 150 min at temperatures with a heating rate of ~ 0.35 K/min starting from ~1250 °C. Two other samples were cooled down after pre-oxidation and used as reference specimens.

To investigate oxide layer degradation phenomena under isothermal conditions, two additional tests were performed in the tube furnace IMF BOX at 1400 °C. For each test two Zry specimens were used: a closed empty cladding sample with a length of 20 mm and a rod sample with a length of 20 mm. The diameter was 10.75 mm in both cases. The samples were pre-oxidised in an argon (50 l/h)–steam (75 g/h) mixture flow at 1400 °C to reach the two desired initial oxide layer thicknesses of 250 and 320 µm, respectively. The following annealing phase lasted 5400 s.

After the tests detailed metallographic analyses were performed.

3. Results and Conclusions

- Reduction of the oxide layer under steam starvation conditions was experimentally investigated with empty Zry-cladding tubes. Two test series with a different initial oxide layer thickness (180 and 240 µm) and different annealing times (40, 90 and 150 minutes) were performed at annealing temperatures of 1250°C - 1350°C under non-isothermal conditions.
- The thickness of "thick" oxide layer (240 µm initially) did not change during the annealing in one direction: a decrease up to ~120 µm was followed by an increase up to ~160 µm.
- Development of the two-phase structure in the oxide layer during the reduction process was observed. The bulk metallic precipitates α-Zr(O) were formed inside of the oxide layer. The content of the metallic phase in the oxide layer reached 10%.
- The scale thickness of the α-Zr(O) scale on the outer surface of oxide layer reached 35 µm after annealing during 9000 s.
- Similar formation of the bulk α-Zr(O) precipitates inside of the oxide layer and development of α-Zr(O) scale on the oxide layer outer surface were observed under isothermal conditions at 1400 °C and 1450 °C.
- Development of the bulk precipitates is more intensive under non-isothermal conditions.

4. Relevant Publications

[1] G. Schanz. "Recommendations and supporting information on the choice of zirconium oxidation models in severe accident codes". Wissenschaftliche Berichte, FZKA-6827 (März 2003)

[2] P. Hofmann, V. Noack, M.S. Veshchunov, A.V. Berdyshev, A.V. Boldyrev, L.V. Matweev, A.V. Palagin, V.E. Shestak. „Physico-chemical behavior of Zircaloy fuel rod cladding tubes during LWR severe accident reflood". Wissenschaftliche Berichte, FZKA-5846 (Mai 97)

[3] J. Stuckert, U. Stegmaier, "Degradation of the cladding oxide layer under steam starvation conditions". Program Nuclear Safety, 2002 Annual Report, Forschungszentrum Karlsruhe, FZKA 6861 (2004)

[4] J. Stuckert, U. Stegmaier, "Behaviour of the cladding oxide layer under steam starvation conditions". 9th Internat. QUENCH Workshop, Karlsruhe, October 13-15, 2003. Proc.on CD-ROM.

[5] J. Stuckert; M. Steinbrück; U. Stegmaier; A. Palagin. „On the thermo-physical properties of Zircaloy-4 and ZrO_2 at high temperatures". Wissenschaftliche Berichte, FZKA-6739 (Oktober 2002)