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EXPERIMENTS ON AIR INGRESS DURING SEVERE ACCIDENTS

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ABSTRACT

Various kinds of experiments on the oxidation of Zircaloy-4 cladding material in different scales and under different conditions at temperatures 800-1300 °C (small scale) and up to 2000 °C (large scale) are presented. The focus of this work was on prototypic mixed air-steam atmospheres and sequential reaction in steam and air, where no data were available before. The separate-effects tests were performed to support the large scale bundle test QUENCH-10 and to deliver first data for model development.

1. INTRODUCTION

Most investigations of core degradation during severe nuclear reactor accidents have considered oxidation of metal core components by steam only. However, there are various scenarios where air may have access to the core. So, air ingress is possible under shutdown conditions when the reactor coolant system is open to the containment atmosphere. Air oxidation of the remaining outer core regions after reactor pressure vessel failure in the late phase of core degradation during severe accidents was identified to be another possible scenario (Powers, 1994). Furthermore, the failure of a storage or transportation cask may result in air intrusion and consequent interaction with the spent fuel rods.

The special impact of air ingress on reactor safety is due to:

- the vigorous oxidation and degradation of the remaining cladding. Zr oxidation by air releases about 85% more heat than oxidation by steam. The oxidation kinetics in air is much faster due to the formation of non-protective oxide (nitride) scales,
- the oxidation of the UO_2 fuel to U_3O_8, leading to lower melting temperature and impairment of the mechanical stability of the fuel, and
- its influence on the volatility of the fission products. So, in highly oxidizing atmosphere, the formation of volatile ruthenium oxides is preferred.

Experimental and analytical work on air ingress was performed within the EC OPSA project (Shepherd, 2000). Recently, this topic is again under examination in the USA with emphasis on storage and transportation cask accidents (Natesan, 2003) and in Europe focusing on shutdown scenarios and the late phase of severe accidents (Giordano, 2003).

The available experimental data on air oxidation are limited to the reaction in pure air. The more prototypical scenarios of air oxidation of steam pre-oxidized zirconium alloys and their reaction in mixed air-steam atmospheres have not been investigated at all. This report presents first results of investigations on air oxidation under such conditions obtained in a large scale bundle test at temperatures

1500-2000 °C and in parametric small-scale separate-effects tests in the temperature range 800-1300 °C.

2. BUNDLE TEST QUENCH-10

Experiment QUENCH-10 (QUENCH-L1) on air ingress conducted at the Karlsruhe Research Center on 21 July 2004 was the first of two experiments to be performed in the frame of the EC supported LACOMERA program. It was proposed by AEKI Budapest, Hungary, and defined together with the Karlsruhe Research Center, supported by Paul Scherrer Institute (PSI), Switzerland. The main objective of this test was to examine the oxidation and nitride formation of Zircaloy during air ingress and the behavior of the degraded bundle during flooding with water.

2.1 The QUENCH facility

The main component of the QUENCH test facility (e.g. Sepold, 2004, Steinbrück, 2004a) is the test section with the test bundle. The bundle is made up of 21 fuel rod simulators approximately 2.5 m long. 20 fuel rod simulators are heated over a length of 1024 mm. Heating is electric by 6 mm diameter tungsten heaters installed in the rod centre and surrounded by annular ZrO_2 pellets to simulate fuel pellets. The bundle geometry and most other bundle components (Zry-4 cladding, grid spacers) used are prototypical for Western type PWRs. The central rod is unheated and is used for instrumentation or as absorber rod. The heated rods are filled with He at a pressure of approx. 0.22 MPa to allow for test rod failure detection by the mass spectrometer. The system pressure in the test section is around 0.2 MPa.

Four Zircaloy corner rods are installed in the bundle to improve the thermal hydraulic conditions. They are also used for additional thermocouple instrumentation and/or can be withdrawn from the bundle during the test to check the amount of oxidation at test phases of special interest. The test bundle is surrounded by a shroud of Zircaloy, a 37 mm thick ZrO_2 fiber insulation, and a double-walled cooling jacket of stainless steel. The shroud acts as gas tight encasement of the bundle and simulates surrounding fuel rods in a real fuel element. The whole set-up is enclosed in a steel containment.

For temperature measurements the test bundle, shroud, and cooling jacket are extensively equipped with thermocouples at different elevations and orientations. Additionally, the test section is provided with various pressure gauges, flow meters, and level detectors. Hydrogen and other gases are analyzed by a state-of-the-art mass spectrometer Balzers GAM300 located at the off-gas pipe about 2 m behind the test section.

2.2 Conduct and main results of experiment QUENCH-10

QUENCH-10 was the first experiment with air ingress. Therefore, extensive pre-test calculations were performed to define test conduct (Homann, 2005). On this basis, the experiment was conducted with the following test phases:

1) Stabilization at 600 °C (axial maximum), facility checks
2) First transient, heating-up to 1350 °C
3) Pre-oxidation of the bundle in Ar-steam at 1350-1420 °C
4) Intermediate cooling to 920 °C
5) Air ingress and transient heat-up
6) Quenching of the bundle by 50 g/s water from the bottom

During the first four phases 3 g/s superheated steam and during the whole test 3 g/s argon as carrier gas for the gas measurement flowed from the bottom to the top through the bundle. The pre-oxidation resulted in a maximum oxide scale thickness of 500 µm, up to the end of this phase 46 g hydrogen were released. To achieve an adequate duration of the air ingress phase, the bundle was cooled to a temperature of 920 °C by decreasing the electrical power input.

For air ingress the steam flow of 3 g/s was replaced by 1 g/s of air. This change in flow conditions had the immediate effect of reducing the heat transfer so that the temperatures began to rise again. The oxidation reaction became faster with rising temperature and complete consumption of oxygen as well as partial consumption of nitrogen (0.1 g/s) were observed toward the end of this phase. The total uptakes of oxygen and nitrogen were 84 and 8 g, respectively. At the end of the air ingress phase, about 0.3 g of hydrogen was released, i.e. approximately at the time when oxygen starvation was observed.

Reflood with 50 g/s water was initiated when the maximum temperatures have reached 1910 °C. Right at the beginning of the quench phase short and mild temperature escalations in the upper part of the bundle were observed. However, cooling was established almost immediately, and complete quenching of the bundle was achieved after about 150 s. A modest release of hydrogen (5 g) was observed during the early phase of reflood, additionally, 3.5 g nitrogen previously taken up was released.

Two corner rods were withdrawn during the test: One at the end of the pre-oxidation phase and one at the end of the air ingress phase. Figure 1 presents the oxide scale thickness distribution at these two rods as an indicator for the oxidation status of the bundle during those times.

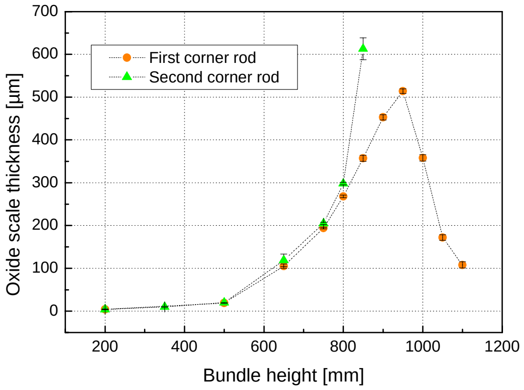

Figure 1: *Axial oxide scale distribution of the corner rods withdrawn at the end of the pre-oxidation phase (1) and at the end of the air ingress phase (2)*

2.3 Post-test appearance of the bundle

After the experiment, the QUENCH-10 bundle and its shroud appear severely damaged, i.e. completely oxidized in the region between 750 and 1000 mm, as can be seen in Fig. 2. Besides oxidation, the shroud exhibits deformation, formerly molten zones, and partly interaction with the ZrO_2 fiber insulation. During handling shroud and bundle were additionally damaged when pieces of shroud and bundle components fell off.

Figure 2: *Post-test appearance of the QUENCH-10 bundle*

The inner surface of the shroud shows a white oxide layer and some spots where Zr nitride seems to have formed by oxidation in air. Golden-appearing nitride phases were also found at the outer surface of second corner rod withdrawn from the bundle at the end of the air ingress phase (Fig. 3).

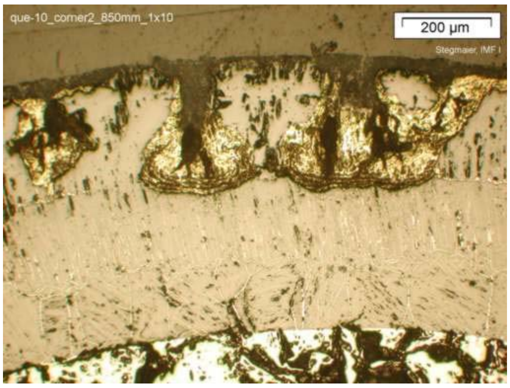

Figure 3: *ZrN formation in the oxide scale of a withdrawn corner rod at the end of the air ingress*

The bundle was embedded in epoxy resin and cut into slices. The post-test examination is not yet completed, however, first examinations revealed the formation of cladding debris beds relocated from the top to the mid of the bundle. So, no cladding material could be found anymore in the hot zone at axial elevation 950 mm. Such a strong embrittlement and debris formation has never seen before in the quench tests with only steam oxidation.

3. SEPARATE-EFFECTS TESTS ON AIR OXIDATION OF ZIRCALOY-4 PRE-OXIDIZED IN STEAM

Various test series were performed in a single rod test rig to support the preparation and analysis of the QUENCH bundle test. Parametric tests allowed for the determination of interim bundle statuses at different bundle elevations and after different phases of the integral test. More generally, these were after early experiments of Leistikow (1988) the first more detailed tests on air oxidation following pre-oxidation in steam.

3.1 Experimental setup, specimens, and test matrix

These experiments were conducted in the QUENCH-SR test rig (Hofmann, 1999). The specimens, consisting of 15 cm long Zircaloy cladding tube segments filled with ZrO_2 pellets, are vertically suspended in a quartz tube. Heating is provided by an induction coil around the quartz tube. Temperature is controlled by a pyrometer and additionally measured by one internal thermocouple in the center of the pellet stack and one external thermocouple fixed to the cladding surface. Argon, air, and steam (for pre-oxidation and with high rate for quenching) are injected by a sophisticated supply system at the bottom of the test section. The off-gas composition is analyzed by a quadrupole mass spectrometer.

The test conducts, i.e. temperature pattern and gas flow rates, were defined on the basis of pre-test calculations for various bundle elevations. The tests started with a pre-oxidation phase in steam-argon at slightly increasing temperatures in order to keep the oxidation rate constant, followed by a constant temperature phase (at 1030, 1130, 1230, and 1300 °C) in argon-air or Ar-N_2 respectively and cooling down in argon or in steam respectively. One additional reference series at 1200 °C was performed without pre-oxidation. Reactions in pure nitrogen were to simulate oxygen starvation conditions, expected to be existent in the upper part of the bundle. In each of the series, the experiments were stopped after pre-oxidation, air or nitrogen reaction, and cooldown phase, respectively, giving altogether a number of 23 tests. Figure 4 gives a schematic overview of the test conditions for these samples with respect to temperatures and times.

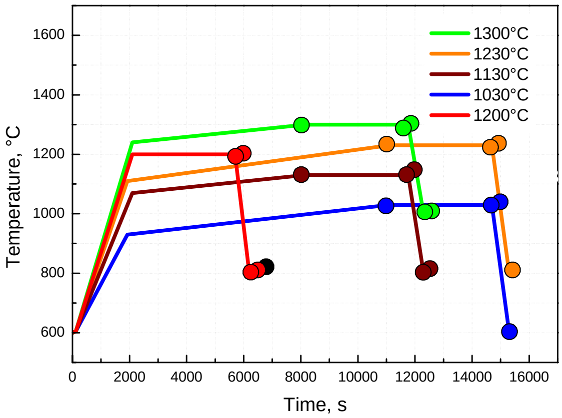

Figure 4: *Schematic test conduct with respect to temperatures and durations. Specimens investigated are marked by symbols*

3.2 Main results

An extensive metallographic post-test examination was performed in order to understand the influence of the air or nitrogen on the integrity of the ZrO_2 layer previously formed in steam. In the frame of this paper, only some examples and a summary can be given.

The reference test with one hour isothermal oxidation at 1200 °C of a bare (not pre-oxidized) Zircaloy specimen in air revealed the well known formation of an oxide scale with strong local degradations caused by the formation and re-oxidation of the less dense zirconium nitride (Krauss, 1999). Nitride precipitates were observed in the boundary region between metal and oxide. This two phase oxide-nitride region is characterized by large pores and circumferential cracks formed due to the different densities of the two phases. The reaction of bare alloy in pure nitrogen resulted in a superficial ZrN layer which is dense near the metal and tends to flake off near its surface. This layer was completely converted to oxide during cooldown in steam giving a 2-3 thicker ZrO_2 layer than the cooldown in steam of a bare Zircaloy specimen from the same temperature.

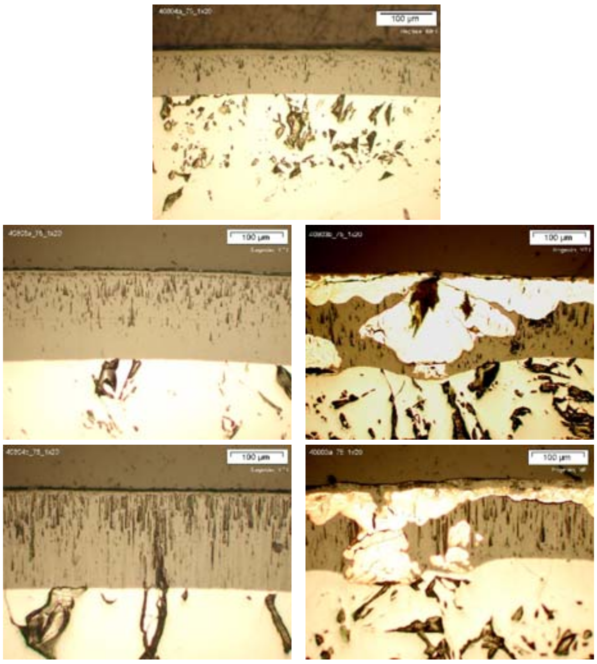

Figure 5: *Metallographic images of specimens after pre-oxidation in steam (top), subsequent air oxidation (mid, left), and quench (bottom, left) as well as subsequent reaction in nitrogen (mid, right) and quench (bottom, right) for test series at 1130 °C*

All other test series were performed with pre-oxidation in steam (Fig. 4). In the following the representative results of the series at 1130 °C are presented in more detail and only special features and differences of the other test series are described afterward.

The appearance of the specimens after the tests at 1130 °C revealed irregularities in color and surface smoothness only for the specimens which were kept in nitrogen atmosphere for a certain time. Especially the cladding tube surface after quench is of yellowish white color and the surface of both nitrogen samples is full of spots and bumps. The axial change of surface appearance follows the axial temperature distribution during the tests.

The metallographic images shown in Fig. 5 confirm that the oxide scale formed under steam is further grown but not degraded during subsequent oxidation in air and quenching. On the other hand, a significant nitride formation is observed for the specimens allowed to react with pure nitrogen to simulate oxygen starvation conditions. The nitride phase has preferably formed near the oxide surface and in cracks in the oxide layer. In lower elevations, where the temperature was a bit lower, huge two-phase oxide-nitride regions were observed (Fig. 6). During quenching the superficial nitride scale was partially re-converted into oxide.

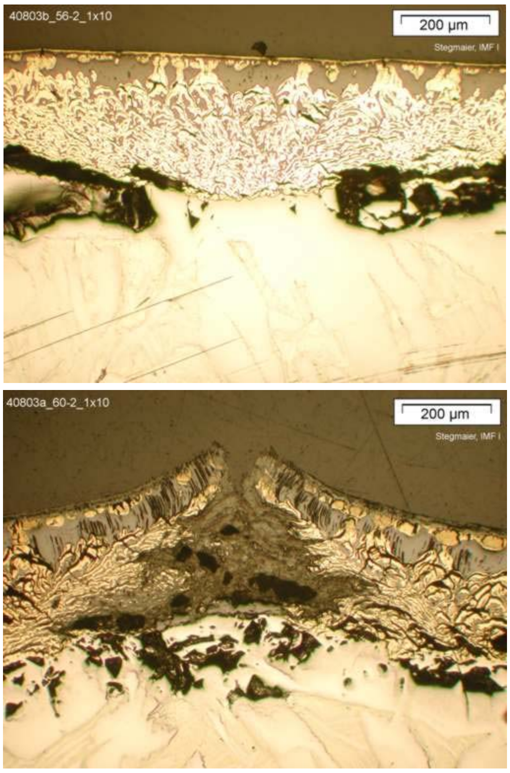

Figure 6: *Typical mixed oxide/nitride regions of steam pre-oxidized specimens after reaction in air (left) and subsequent quench in steam (right) for test series at 1130 °C*

Very similar effects were observed in the test series at the other temperatures with more pronounced influence of nitrogen at higher temperatures. In most of the tests with air oxidation no nitride phases were found. Only where breakaway effects were observed, nitride was found together with swelling and accelerated growth of oxide layers. Besides the tests at the 1200°C series where no protective oxide scale was formed this was only seen in one of three tests of the 1030°C series with only 24 µm pre-oxidation scale.

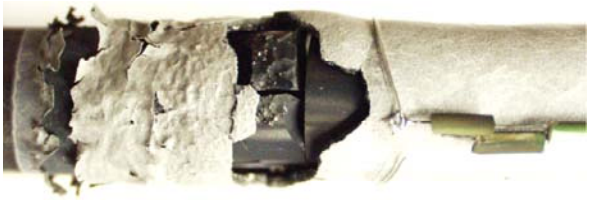

Figure 7: *Fuel rod simulator specimen after pre-oxidation in steam, nitrogen reaction at 1300 °C and quenching in cold steam*

Quenching showed no significant effect in all but one sample. Quenching from the highest temperature after reaction in nitrogen caused almost complete destruction of the specimen (Fig. 7) very similar to what was observed after the bundle test QUENCH-10. This is in agreement with the finding that during the end of the air ingress phase in the bundle test oxygen starvation had established.

4. SEPARATE-EFFECTS TESTS ON OXIDATION OF ZIRCALOY-4 IN MIXED AIR-STEAM ATMOSPHERES

Another, independent test series was performed to investigate the influence of air in more prototypic mixed steam-air atmospheres on the oxidation kinetics.

4.1 Experimental setup, specimens, and test matrix

These experiments were conducted in the so-called BOX rig (Steinbrück, 2004b). The main part of this test facility is an electrically heated horizontal tube furnace coupled with a sophisticated supply system for various gases and steam at the inlet and with a mass spectrometer for quantitative analysis of the off-gas composition at the outlet. All steam-carrying parts and tubes are heated for quantitative determination of the steam concentration. The oven was extended by a sample air lock for the recent tests to allow for specimen change with furnace at temperature, and therefore, higher sample throughputs and fast cool-down of the specimen.

2 cm long Zircaloy-4 cladding tube specimens were suspended at a thin zirconia tube, thus, enabling inside and outside oxidation of the tube segments.

So far, 45 isothermal tests with 1 h duration have been performed at temperatures 800, 900, 1000, 1100, and 1200 °C under nine different steam-air mixtures at total flow rates of 100 l/h including pure air and pure steam. The specimens were pushed into the reaction tube at temperature under inert conditions, and the atmosphere was changed to the desired reaction mixture after stabilization of the temperature. At the end of the test the atmosphere was changed again to pure argon, before the specimens were pulled out of the oven into the cold air lock.

4.2 Main results

As could be expected from chemical thermodynamics, during these experiments in mixed atmospheres the oxidation in oxygen is in favor in comparison with the oxidation in steam. Hydrogen was only released in tests under pure steam or in case of oxygen starvation. So, the oxygen was completely consumed after initiation of air-steam inlet during the tests at 1100 and 1200 °C, thus putting the steam in the position to be oxidizing agent in the competing reaction of the both gases. These starvation periods lasted between 320 s for the 1200 °C test with the lowest air concentration (2.6%) to only a very few seconds in the tests at 1100 and 1200 °C under 50%-50% air-steam mixtures.

At 800 °C, air addition to steam had no effect on the oxidation, which was recognized by mass gain measurement (see Fig. 8) and post-test metallographic examinations. Only pure air led to an accelerated oxidation kinetics caused by the formation of less protective oxide scales with circumferential cracks. At 900 °C, a significant effect of air on the formation of more degraded oxide scales was seen with 90% air, whereas lower air concentrations in the mixture had almost no effect on mass gain and quality of the oxide scale.

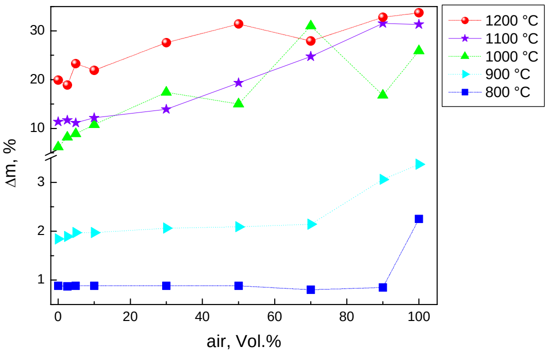

Figure 8: *Mass gain after one hour isothermal oxidation in air-steam mixtures at 800-1200 °C*

A more gradual change of the oxidation and degradation status of the samples was observed after the tests at 1000, 1100, and 1200 °C. Here, even low amounts of air addition to steam caused an enhanced degradation of oxide scales and higher oxidation kinetics, as could be seen in Fig. 9 as example. Mixed oxide/nitride phases were seen between the metal and oxide scales. Obviously, the nitrides primarily formed at the metal/oxide interface are subsequently oxidized which causes, due to the different densities of ZrN and ZrO_2, the formation of non-protective scales.

Breakaway effects (Schanz, 1981) were observed in all tests at 1000 °C, independent of the composition of the atmosphere. So, in the experiment under pure steam, the hydrogen release starts to increase again after about 40 min indicating the loss of protective effect of the oxide scale due to crack formation and spalling. The same was seen in the experiments with air in the atmosphere; here the oxygen concentration in the off-gas was reduced after a certain time in the tests. Breakaway is also thought to be the reason for the irregularities in the mass gain curve of the 1000 °C test series in Fig. 8.

These first exploratory experiments will be extended by more quantitative tests on oxidation kinetics in mixed atmospheres.

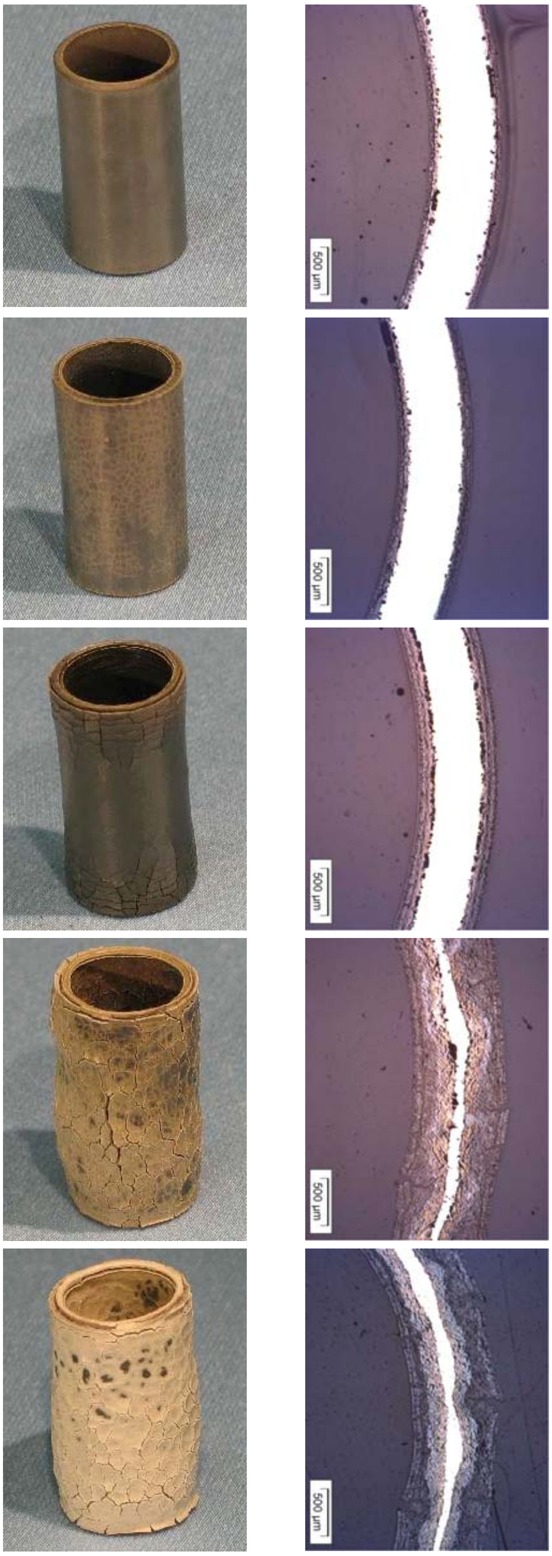

Figure 9: *Post-test appearance (left) and cross section (right) of Zircaloy-4 specimens after 1 h isothermal oxidation at 1000 °C in mixed air-steam atmosphere with the following air concentrations (from top to bottom): 0, 3, 30, 70, 100%*

5. SUMMARY AND CONCLUSIONS

The various experimental results presented here for the first time, reveal the strong effect of air on the oxidation and degradation of Zircaloy cladding tubes. So, such a strong degradation with debris formation and relocation below the melting temperature of the cladding and without absorber material was never observed before in any other QUENCH bundle test. On the other hand, despite the heavy degradation of the bundle QUENCH-10 only low amount of hydrogen was released during the quench phase.

The separate-effects tests delivered first data on the oxidation of Zircaloy-4 in mixed air-steam atmospheres and on sequential oxidation in steam and air. In the later tests, it was shown that, at least for the durations chosen here, an intact oxide scale formed under steam continuously grows further and keeps its protective effect under air atmosphere. Otherwise, pure nitrogen atmosphere causes the formation of nitride phases connected with degradation of an oxide scale previously formed under steam. The superficial ZrN scales were partially reconverted into oxide during a final cool-down in steam.

The experiments under mixed air-steam atmospheres revealed an increasing detrimental effect of even low air concentrations with temperature. Whereas at 800 °C addition of air to steam has no influence on the formed oxide scale (within the duration of the experiments and with the exception of pure air), starting from 1000 °C a gradual change of the quality of the oxide scale with composition of the atmosphere was observed. Increasing air content caused stronger degradation of the scale due to the formation of nitride at the metal/oxide interface. Additional breakaway effects were seen only in the 1000 °C independently on the composition of the gas mixture. Hydrogen was only released in tests with pure steam atmosphere and in case of oxygen starvation.

These first exploratory experiments will be extended by more quantitative tests on oxidation kinetics in mixed atmospheres and on air oxidation following steam oxidation in the near future.

ACKNOWLEDGEMENT

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