Cladding oxidation during air ingress. Part I: Experiments on air ingress

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ABSTRACT

Air ingress is a potential risk in some low probable situations of severe accidents in a nuclear power plant. Air is a highly oxidizing atmosphere that can lead to an enhanced Zr-based cladding oxidation and core degradation affecting the release of fission products. This is particularly true speaking about ruthenium release, due to its high radiotoxicity and its ability to form highly volatile oxides in a significant manner in presence of air. The oxygen affinity is decreasing from the Zircaloy cladding, fuel and ruthenium inclusions. It is consequently of great need to understand the phenomena governing cladding oxidation by air as a prerequisite for the source term issues in such scenarios. In the past years, many works have been done on cladding oxidation by air under severe accident conditions.

This paper with in addition the paper "Part II: Synthesis of modeling results" of this journal issue aim at assessing the state of the art on this phenomenon.

In this paper (Part I), the phenomenological approach is based on the analysis of experiments at different scales as separate-effect tests and integral tests like CODEX-AIT (low degree of pre-oxidation, high air flow rate), QUENCH-10 (high degree of pre-oxidation, moderate air flow rate, quench initiation at high temperature), PARAMETER-SF4 (moderate degree of pre-oxidation, low air flow rate, quench initiation at high temperature) and QUENCH-16 (moderate pre-oxidation, very low air flow rate, quench initiation at moderate temperature). The following phenomena will be described: formation of a porous nitride–oxide layer, subsequent steam penetration through this porous layer during reflood, accompanied by nitride re-oxidation and intensive cladding oxidation.

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1. Introduction

In a nuclear power plant (NPP), air penetration to the fuel assembly is a potential risk in some low probability situations of severe accidents. Air ingress is possible under shutdown conditions when the reactor coolant system is open to the containment atmosphere. Another possibility is air oxidation of the outer core regions after reactor pressure vessel failure in the late stage of core degradation during severe accidents (Powers et al., 1994). Furthermore, air ingress into a spent fuel pool after LOCA was discussed already in the seventies (Benjamin et al., 1979), and corresponding discussions were intensified after the Fukushima Daiichi accidents. In comparison with steam, chemical heat release during oxidation in oxygen is 80% higher: at a temperature of 1273 K the oxidation in oxygen ($Zr + O_2 \rightarrow ZrO_2 + 1096$ kJ/mol) results in almost double energy release compared to the oxidation in steam ($Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 + 597$ kJ/mol). This circumstance accelerates the growth

of the surface oxide layer under adiabatic conditions. At high temperatures, an underlying α-Zr(O) layer is simultaneously formed with the oxide growth. The α-Zr(O) regions can be formed also inside the ZrO_2 layer under oxygen starvation conditions (Stuckert and Veshchunov, 2008). Due to different phenomena (e.g. break-away of oxide at lower temperatures or formation of radial cracks in the oxide at higher temperatures) the air penetrates to the cladding metal, where oxygen will be dissolved and nitrogen attacks (also exothermically) the formed α-Zr(O): $2Zr + N_2 \rightarrow 2ZrN + 730$ kJ/mol (at 1273 K). As a result, very porous nitride regions are growing at the metal–oxide interface. These regions are no more barriers for penetration of steam during core reflood. Moreover, the nitrides can be exothermically re-oxidized by steam. Therefore, air is a highly oxidizing atmosphere that can lead (in comparison to pure steam atmosphere) to an accelerated Zr-based cladding oxidation and core degradation affecting the release of fission products. This is particularly true speaking about ruthenium release, due to its high radio-toxicity and its ability to form highly volatile oxides in presence of air. It is consequently of great need to understand the phenomena governing cladding

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oxidation by air as a prerequisite for the source term issues in such scenarios. In the past years, many experimental (described in this paper) and analytical (e.g. Birchley and Fernandez-Moguel (2012)) works have been done on cladding oxidation by air under severe accidents conditions.

Experimental and analytical works on air ingress were performed within the EC 4th and 6th Framework Programs (Albiol et al., 2010). Bundle tests under different conditions (different degree of cladding oxidation, different temperatures, different availability of air) were performed at AEKI/Budapest (CODEX facility), KIT/Karlsruhe (QUENCH facility) and LUCH/Podolsk (PARAMETER facility). The results of these bundle tests are presented in the Chapter 2 of this paper. Two first bundle tests were performed in the CODEX facility with a relatively low pre-oxidation of the claddings, in the absence of global oxygen starvation, and without test termination by water reflood. The formation of zirconium nitrides at several bundle elevations was observed. The influence of different oxide layer thicknesses, full oxygen consumption before the end of the air flow and the re-oxidation of nitrides during the reflood were investigated in the subsequent PARAMETER and QUENCH bundle tests. The importance of cooperative processes in bundles was demonstrated during the OECD/NEA project SFP: strong degradation of full-scale 17 × 17 PWR assemblies after ignition in air was observed (SFP, 2013).

Numerous single-effect tests on cladding oxidation in air were performed at ANL (temperatures 573–1173 K), AEKI (temperatures 873–1773 K), IRSN (temperatures 873–1473 K) and KIT (temperatures 873–1873 K). A brief overview of the corresponding results, important for the model developments, is given in the Chapter 3 of this paper.

2. Bundle tests

A number of bundle air ingress tests have been performed under a range of configurations and oxidizing conditions, namely CODEX AIT-1, AIT-2 with small 9-rod bundles (Hózer et al., 2003), QUENCH-10 with 21-rod strongly pre-oxidized bundle (Stuckert et al., 2004; Schanz et al., 2006; Steinbrück et al., 2006), QUENCH-16 with 21-rod moderate pre-oxidized bundle (Stuckert et al., 2013; Stuckert and Steinbrück, 2014) and PARAMETER-SF4 with finally molten 19-rod bundle (Degtyareva et al., 2009; Konstantinov et al., 2007). The accumulated data have demonstrated that air oxidation of the cladding is a quite complex phenomenon governed by numerous processes depending on the oxidizing conditions, the oxidation history and the details of the cladding material specification.

The main parameters of the bundle tests are summarized in Table 1. The air flow rate is given taking into account the surface of claddings and "effective rods": shroud and corner rods.

2.1. CODEX-AIT-1 and -2 tests

The CODEX facility was built at AEKI/Budapest in 1995 for the investigation of the behavior of small fuel bundles under severe accident conditions. In the AIT tests, nine-rod pressurized water reactor (PWR) type bundles were used. The rods were arranged on a square lattice; eight peripheral rods were electrically heated with tungsten bars. The central rod was not heated, it was filled with annular UO_2 pellets, and the central void was used for instrumentation (Fig. 1). Two Zircaloy-4 spacer grids were installed at elevations −15 and 535 mm to fix the bundle.

The heated length of the bundle was 600 mm. The cladding material was Zircaloy-4; the shroud part was made of a 2 mm thick Zr2%Nb alloy. Inside the fuel rods, annular UO_2 pellets were placed between the tungsten rods and the cladding. Depleted uranium was used; the pellets were not irradiated and contained no additional elements for fission product simulation. ZrO_2 thermal insulation was added around the shroud.

The two CODEX-AIT tests were performed in 1999. Five test stages were used for both tests CODEX-AIT-1 and -AIT-2: (1) preparation at relatively low temperatures, (2) pre-oxidation under transient conditions, (3) cool-down in inert atmosphere to temperatures below 1200 K, (4) air ingress, (5) cool-down in inert atmosphere to room temperature.

CODEX-AIT-1 started with a heating-up period, and stable temperature distribution was reached with peak cladding temperature of about 1200 K (Fig. 2). The pre-oxidation stage was initiated with the reduction of argon flow and injection of oxygen at the same time. Strong temperature excursion took place during the pre-oxidation, which could be stopped only by switching off the power and stopping the oxygen injection. The temperature maximum was 1800 K on the upper spacer grid (535 mm). After this unexpected transient, a cool-down period took place by regulating the power in argon atmosphere. During this stabilization stage one part (about 10 μm) of oxide layer was dissolved due to transport of oxygen into the metallic layer of cladding. The interim cool-down in argon is not typical for a reactor case and was necessary to have stable parameters for the beginning of final degradation stage.

The air ingress stage was initiated at 1173 K maximum temperature with the injection of room temperature air. Argon injection was stopped and power was kept constant. The cold air cooled down the lower part of the bundle (T_{pct} < 1373 K at elevations below 450 mm), but then was heated and led to moderate temperature excursion up to 1773 K in the upper part at the bundle elevation of 570 mm. Then the cool-down stage was initiated by switch off of electrical power, stopping air injection, and injection of cold argon.

The AIT-2 test was planned to proceed to more severely degraded state. The use of steam rather than Ar + O_2 for

Table 1
Parameters of bundle tests with air ingress.

Test	Max ZrO_2 before air ingress, μm	Air flow rate, g/s/ (eff. rod)	Initial T_{pct} at air injection, K	Durations of (air ingress)\(oxygen starvation), s	T_{pct} at reflood/cool-down, K	Nitrides	Hydrogen production during reflood, g
CODEX AIT-1	40 (dissolution from 50)	3.5/(9 + 5) = 0.25	1173	570\NA	2273	Distributed inside ZrO_2 or along α-Zr (O) layer	Cool-down in Ar
CODEX AIT-2	20 (steam + air) + 15 (air leak)	2.5/(9 + 5) = 0.18	1073	800\NA	2173	"Pockets" and layers inside ZrO_2	Cool-down in Ar
PARAMETER SF-4	250	0.5/(19 + 12.6) = 0.016	1173	1476\NA	2110	Dissolved in melt	86
QUENCH-10	500	1/(21 + 9.6) = 0.033	1190	1800\80	2200	Localized "pockets" at outer side of ZrO_2 layer	5 (1 g due to re-oxidation of nitrides)
QUENCH-16	135	0.2/(21 + 9.6) = 0.007	1000	4035\800	1873	Layers distributed inside ZrO_2 layer	128 (7 g re-oxidation of nitrides + 96 g metal oxidation + 25 g melt oxidation)