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The QUENCH Programme at Forschungszentrum Karlsruhe (FZK)

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ABSTRACT

The QUENCH programme at FZK was launched to investigate the hydrogen source term during reflood of an overheated reactor core. It consists of large scale bundle experiments, separate-effects tests, modelling activities and application and validation of severe fuel damage (SFD) code systems. The paper describes the experimental part of the programme, namely the experimental facilities and test rigs as well as selected results obtained during the recent years.

1 INTRODUCTION

Cooling of an uncovered, overheated Light Water Reactor (LWR) core by water is the main accident management measure for terminating a severe accident transient. But, before the water succeeds in cooling the fuel elements, the injected water can, under certain circumstances, trigger an enhanced oxidation of the Zircaloy cladding that causes a rapid increase in temperature and hydrogen generation.

The QUENCH programme at the Forschungszentrum Karlsruhe is to investigate the hydrogen source term resulting from water injection into an uncovered core of a LWR, to examine the physico-chemical behaviour of overheated fuel elements under different flooding conditions, and to create a data base for model development and severe fuel damage (SFD) code improvement. The physical and chemical phenomena of the hydrogen release during reflood are not sufficiently well understood. In particular, an increased hydrogen production during quenching cannot be determined on the basis of the available Zircaloy/steam oxidation correlations. Presently, it is assumed that the following phenomena lead to an enhanced oxidation and hydrogen generation: melt oxidation, steam starvation conditions, and crack surfaces oxidation. In most of the code systems describing severe fuel damage, these phenomena are either not considered or only modelled in a simplified empirical manner.

The large-scale 21 rod bundle experiments in the QUENCH facility, supported by an extensive separate-effects test (SET) programme, modelling activities as well as application and improvement of SFD code systems, are the highlights of the programme. Figure 1 shows the organisational structure of the programme with the various crosslinks between the single elements. SETs are performed to deliver data for model development and validation as well as

to support preparation and analysis of the integral experiments. On one hand, SFD codes are extensively used in pre- and post-test calculations for the bundle experiments whose results on the other hand are important for code validation.

On the next few pages, the two experimental parts of the programme are briefly described together with some highlights of the results obtained during the recent years.

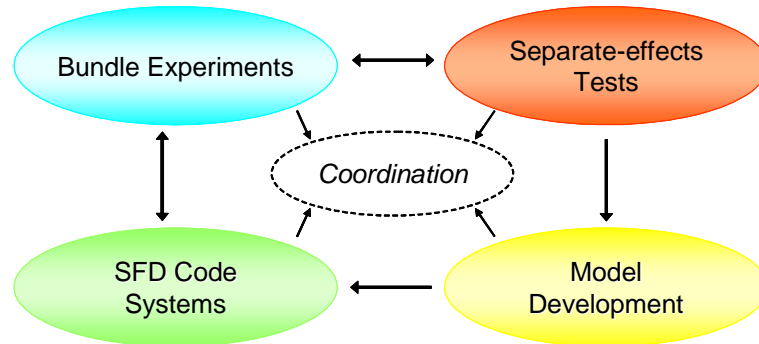


Figure 1: Organisational structure of the QUENCH programme at FZK

2 QUENCH BUNDLE TESTS

2.1 Design of the QUENCH facility

The main component of the QUENCH test facility is the test section with the test bundle (Fig. 2). Superheated steam from the steam generator and superheater together with argon as a carrier gas enter the test bundle at the bottom. The argon, the steam not consumed, and the hydrogen produced in the zirconium-steam reaction flow from the bundle outlet at the top through a water-cooled off-gas pipe to the condenser where the steam is separated from the non-condensable gases argon and hydrogen. The system pressure in the test section is around 0.2 MPa. QUENCH experiments can be terminated either by quenching with water from the bottom or from the top or by the injection of cold steam from the bottom.

The test bundle is made up of 21 fuel rod simulators approximately 2.5 m long (Fig. 3). 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 ZrO₂ pellets. Electrodes of molybdenum and copper connect the heaters with the cable leading to the DC electric power supply (70 kW). The central rod is unheated and is used for instrumentation or as absorber rod. The fuel rod simulators are held in position by five grid spacers, four are made of Zircaloy and the one at the bottom of Inconel. The rod cladding of the heated fuel rod simulator is identical to that used in LWRs with respect to material and dimensions (Zircaloy-4, 10.75 mm outside diameter, 0.725 mm wall thickness). The heated rods are filled with Ar-5%Kr or He at a pressure of approx. 0.22 MPa. The krypton or helium additive allows test rod failure to be detected by the mass spectrometer.

Four Zircaloy corner rods are installed in the bundle. Three of them are used for thermocouple instrumentation whereas the fourth rod can be withdrawn from the bundle to check the amount of oxidation before the quench phase. The test bundle is surrounded by a shroud of Zircaloy with a 37 mm thick ZrO₂ fibre insulation up to the upper end of the heated zone and a double-walled cooling jacket of stainless steel up to the upper end of the test section.

Hydrogen is analyzed by two different methods: (1) a state-of-the-art mass spectrometer Balzers GAM300 located at the off-gas pipe about 2 m behind the test section, and (2) a commercial-type hydrogen detection system "Caldos 7G" located behind the off-gas pipe and

condenser. For temperature measurements the test bundle, shroud, and cooling jackets are extensively equipped with thermocouples at different elevations and orientations.

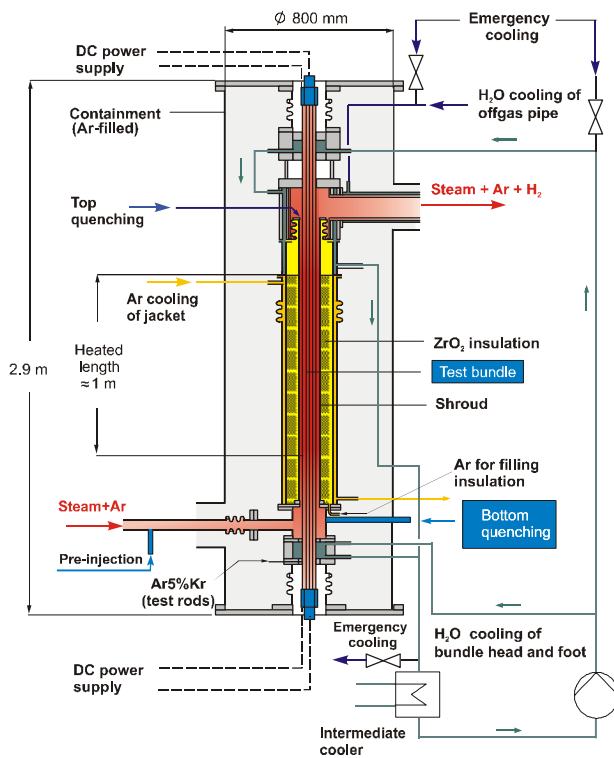


Figure 2:

QUENCH test section with test bundle and flow paths. The quenching water is injected through a separate line marked "Bottom quenching," whereas the cooling steam enters the test section through the same line as the superheated steam in the phases prior to reflooding.

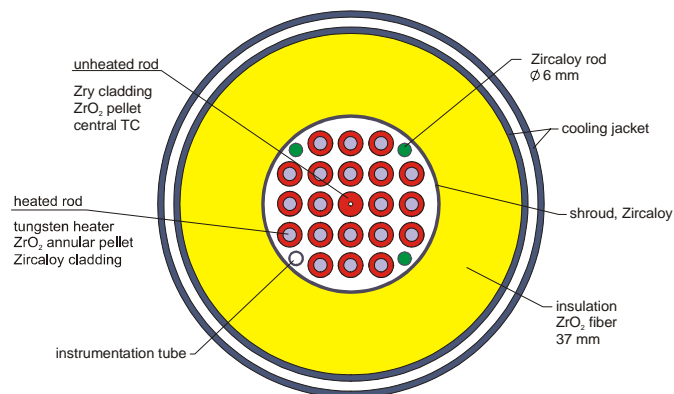


Figure 3:

Cross section through the test bundle, shroud, insulation and cooling jacket

2.2 Test matrix

So far, ten tests have been performed since the commissioning of the facility in 1997. The main experimental parameters investigated were: 1) the temperature at initiation of reflood, 2) the degree of pre-oxidation, 3) the quench medium, i.e. water or steam, 4) the influence of a B₄C absorber rod, 5) the effect of steam starved conditions before quench as well as 6) the influence of air oxidation on the materials behaviour and hydrogen source term during quench. Table 1 gives an overview on the main parameters and results of the QUENCH bundle experiments.

In the first six tests, different bundle and flooding conditions with PWR type bundle without additional absorber materials were investigated. The effect of B₄C absorber rods was

studied in experiments QU-07 to QU-09. Additionally, steam starvation conditions were achieved in test QU-09. Finally, the last test QU-10 was to investigate the behaviour of a fuel bundle during air ingress in a spent fuel pool accident with the main objective to examine the oxidation and nitride formation of Zircaloy in air. Some important results of these experiments are given in the next chapter.

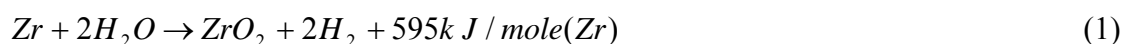
Table 1: Test conditions and main results of QUENCH bundle tests

Test Date	Quench medium	Initial temp. [K]	Flooding rate [g/s]	Significant melt form.	Max. ZrO ₂ scale [μm]	H ₂ release before/during reflood [g]	Remarks
QUENCH-01 Feb 26, 98	water	≈ 1830	52	no	≈ 300	36 / 3	EC COBE pre-ox. reference
QUENCH-02 Jul 07, 98	water	≈ 2470	47	yes	Cladding completely oxidized	20 / 140	EC COBE reference
QUENCH-03 Jan 20, 99	water	≈ 2450	40	yes	Cladding completely oxidized	18 / 120	Q-02/delayed reflood
QUENCH-04 Jun 30, 99	steam	≈ 2110	50	no	≈ 170	10 / 2	steam reference
QUENCH-05 Mar 29, 00	steam	≈ 2020	48	no	≈ 400	25 / 2	Q-04/preox
QUENCH-06 Dec 13, 2000	water	≈ 2060	42	no	≈ 660	32 / 4	OECD ISP-45 Q-05/water quench
QUENCH-07 Jul 25, 01	steam	≈ 2100	15	yes	Cladding completely oxidized	62 / 120	EC COLOSS B ₄ C absorber
QUENCH-08 Jul 24, 03	steam	≈ 2070	15	no	Cladding completely oxidized	46 / 38	Q-07 reference test without absorber
QUENCH-09 Jul 03, 02	steam	≈ 2100	49	yes	Cladding completely oxidized	60 / 400	EC COLOSS Q-07/steam starvation
QUENCH-10 Jul 21, 04	water	≈ 2180	50	tbd.	tbd.	47 / 5	EC LACOMERA air ingress

Some of the QUENCH bundle experiments were supported by the European Commission within the Fourth and Fifth Framework Programme. Test QU-06 was selected as OECD international standard problem ISP-45.

2.3 Selected results

The main objective of the QUENCH programme is the determination of the hydrogen source term during reflood of an overheated reactor core. Hydrogen is mainly produced by the exothermal chemical reaction between the zirconium alloy cladding and water/steam according to Eq. (1).



The rate of this reaction increases exponentially with temperature, i.e. it is described by Arrhenius' law. The water injected for reflood acts as a coolant, but at the same time it is an oxidant, which is available in abundance during that phase. The change of the energy balance during the quench phase compared to that before quench initiation determines if water injection leads to an immediate cool-down of the bundle or to an escalation of temperatures

connected with strongly increased hydrogen and fission product (in real fuel element of a NPP) releases.

Table 1 shows that both types of behaviour were observed in the bundle experiments. The hydrogen release before the quench phase (as an integral measure for the pre-oxidation of the bundle) as well as the hydrogen produced during reflow are compiled in the last but one column of the table. In some of the tests, only few grams of hydrogen were produced by the injection of the quench water or steam, whereas in other tests two orders of magnitude higher amounts of hydrogen were released during this phase. Figure 4 gives the results on temperatures and hydrogen release of experiments QU-04 and QU-07 without and with temperature escalations as an example.

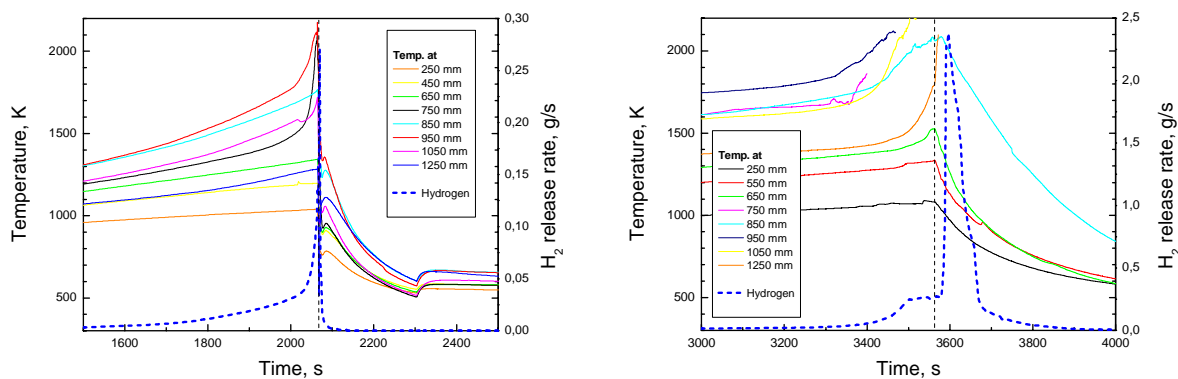


Figure 4: Selected temperatures and hydrogen release rate during quench phase of tests QU-04 (left) and QU-07 (right)

The bundle experiments performed so far have shown that cracking and/or spalling of oxide scales connected with the formation of fresh metallic surfaces does not play such an important role as thought at the beginning of the programme. On the other hand, the presence of metallic melts seems to trigger escalations because their oxidation is much faster than the oxidation of the solid components (see also chapter 3.2). Melts are formed when the temperature is high enough, i.e. above 2130 K for β -Zr (2030 K for Zry-4) and \sim 2400 K for the oxygen stabilised α -Zr(O). Additionally, eutectic interactions between the various components in the core may lead to melt formation far below the melting points of the single components. So, melt formation takes place very rapidly in B₄C absorber rods at temperatures above 1500 K due to eutectic interactions between B₄C and the steel cladding and between steel and the Zircaloy guide tube.

Figure 5 demonstrates this effect by comparing post-test bundle cross-sections of one test with boron carbide absorber rod (QU-07) and the reference test without absorber rod (QU-08). Significant amounts of melt have been formed and relocated even to the relatively cold elevation of the grid spacer at 550 mm during test QU-07. At 750 mm, the central absorber rod reveals absorber melt kept in the gap between an outer ZrO₂ scale of the guide tube and the partially consumed B₄C pellet. The control rod is completely gone at the hottest elevation 950 mm. The bundle QU-08 without absorber rod looks quite different, although the test conditions were very similar. No significant melt is formed in the bundle. Only the Zircaloy shroud shows melt formation in the hottest zone, indicating that the temperatures there were between the melting temperatures of β -Zr which was still available in the thick shroud tube wall and α -Zr(O) to which the thinner cladding tubes were converted at the end of the test.

Test bundle QU-09 was equipped with a B₄C absorber rod but additionally a steam starvation phase was introduced before quench in order to make the test comparable to the French Phebus FPT-3 in-pile test, planned to be performed in autumn 2004. This procedure led to the highest hydrogen production ever observed in the QUENCH bundle tests and a complete melting and oxidation of all bundle components over a length of about 1 m. It is plausible to attribute the escalation mainly to the effects of the steam starved phase on the protection of the oxide scales (see Chap. 3). Moreover, a delayed release of absorber melt, observed in comparison with QU-07 can have led to more violent melt dispersion and oxidation at more elevated temperature levels.

The most recent test QU-10 included an air ingress phase before quench. It seems that the air inlet after strong steam pre-oxidation did not cause an excursion of temperatures and hydrogen production during reflood, but a strong embrittlement of the cladding.

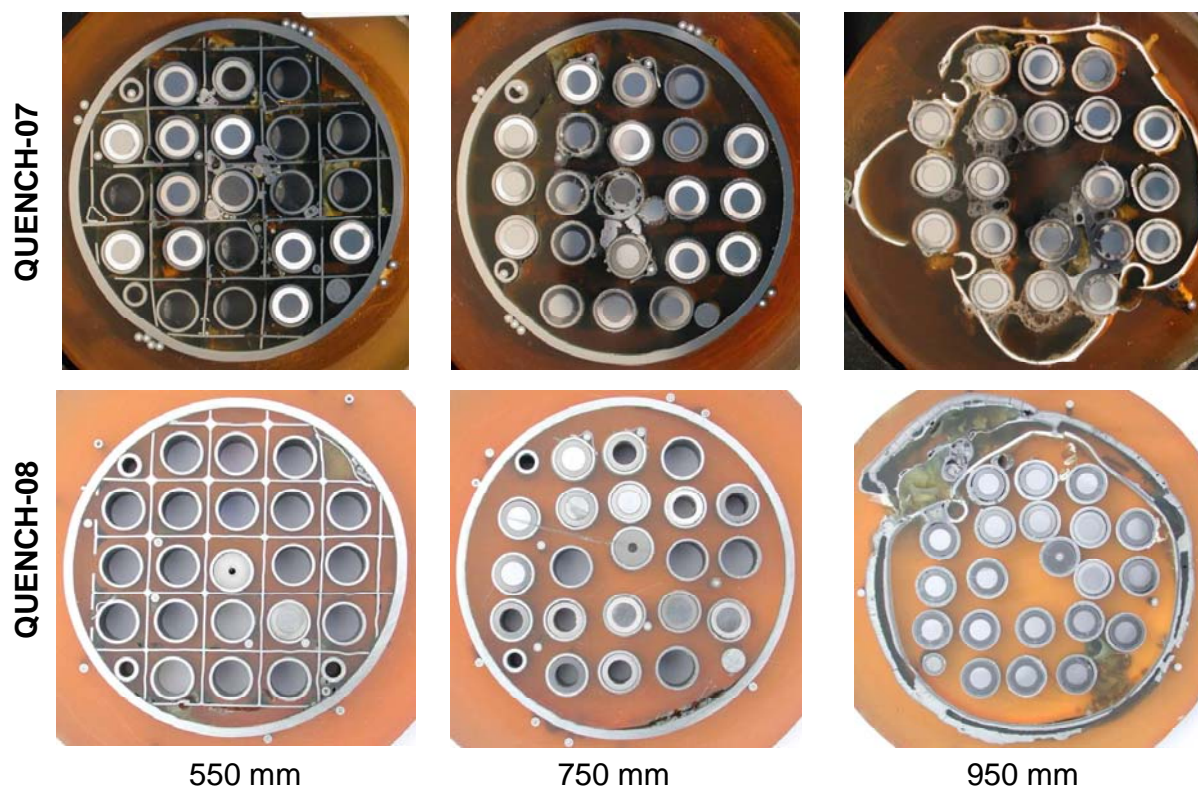


Figure 5: Post-test cross sections of tests QU-07 with absorber rod (top) and QU-08 without absorber rod (bottom)

2.4 Computational and analytical support

From the start of the programme, the bundle tests were accompanied by computational support at FZK, mainly with the in-house version of SCDAP/RELAP5 (S/R5), where special features of the facility are included. In this way, the design of the test section could be improved substantially before its construction and commissioning. Pre-test calculations, taking into account the facility up to and including the containment, were performed for all tests. They had several aims: to guarantee the safety of the facility, to derive a test protocol that fulfils the aims of the test, to determine important parameters of the test like the power history and the fluid composition, and to assess the sensitivity of the facility, when test conditions are changed. This work was supported by nuclear power plant calculations to assure that the test protocol is as representative for reactor conditions as possible. Post-test

calculations helped understanding the tests, getting parameters that cannot be measured directly, and assessing the quality of the experimental data.

Bundle test QUENCH-06 was a basis for International Standard Problem no. 45 (ISP-45) of OECD, hosted at FZK. After the test, blind calculations were performed by participants of 21 organizations from 15 countries, where only the absolute minimum of information (specification of the facility, boundary, and initial test conditions) was made available to the participants. Up to the start of the quench phase, the results of most participants did not differ much, but during the quench phase thermal hydraulic aspects of the test caused some problems. Examination of the results showed further that the energy balance was not fulfilled in all cases. In a second, open phase, the entire experimental database was made available, and 10 participants delivered improved results after removing errors or improving the code. As a general outcome, user effects may have a larger influence on the results than modelling differences in the codes, and transfer of knowledge to inexperienced collaborators is an important task, about which all involved persons, including managers, should be aware of.

3 SEPARATE-EFFECTS TESTS

3.1 Experimental set-ups

Different experimental setups are used to support the bundle tests and to deliver data for model development. These test rigs are complementary with respect to heating method (induction or resistance), maximum temperatures, sample dimensions, and reaction atmospheres, as can be seen in Fig. 6. Specimens can be either directly heated by induction (QUENCH-SR) or indirectly using a tungsten susceptor (LAVA).

The QUENCH-SR (Single Rod) rig is equipped with a quench system allowing flooding specimens by water from temperatures up to 2000 K. The highlight of the BOX rig is the gas and steam supply system which accurately delivers any desired reaction atmosphere over long durations.

All furnaces are coupled with a high-performance quadrupole mass spectrometer for qualitative and quantitative analyses of the gaseous reaction products. Mass changes during oxidation reactions can be measured by a thermo-balance system (TG).

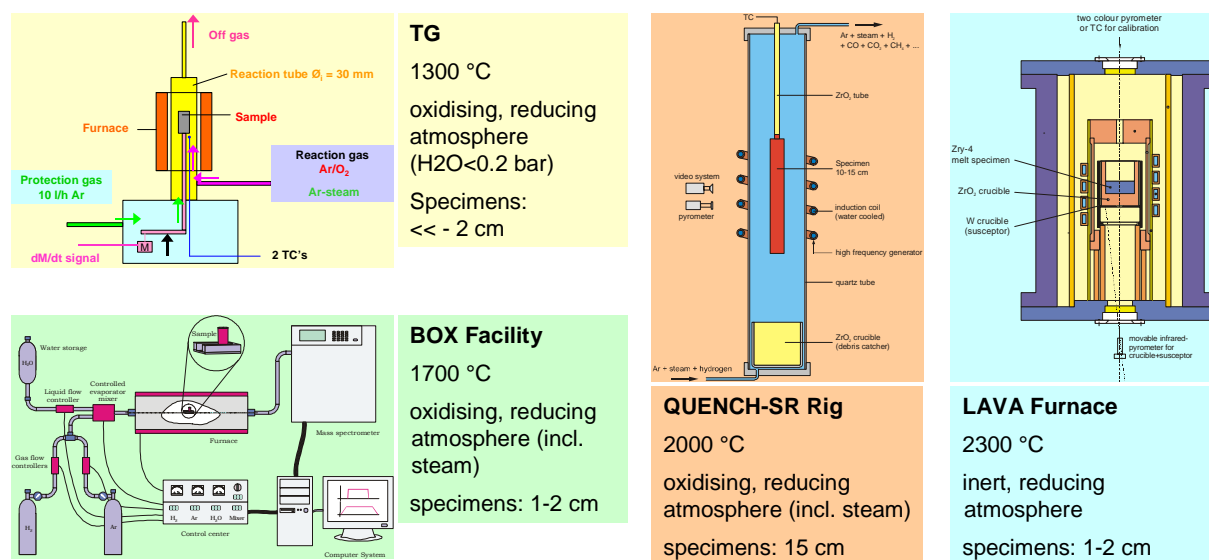


Figure 6: Setups for separate-effects tests in the QUENCH programme. Maximum working temperatures, possible atmospheres and specimen dimensions

3.2 Topics and selected results

The following topics on high-temperature oxidation and materials interactions have been investigated in the recent years:

- Quench behaviour of Zry-4 and Zr1Nb cladding tubes
- Hydrogen absorption by zirconium alloys
- Failure criteria of a ZrO_2 scale at the cladding surface during temperature transients
- Dissolution kinetics of zirconia and urania in Zircaloy melts
- Oxidation kinetics of boron carbide and absorber melts
- Degradation of B_4C control rods
- Degradation of oxide scales during steam starved conditions
- Oxidation of cladding materials in air and steam/air atmospheres

Much more work in this field was done in the 1980s and 1990s at Forschungszentrum Karlsruhe (FZK, formerly Kernforschungszentrum Karlsruhe, KfK), which is outside the scope of this paper. Even from the topics mentioned above, only some selected results can be presented here.

Single rod quench tests

Single-rod quench tests with Zircaloy-4 cladding tube segments have shown a clear correlation between the degree of pre-oxidation at the onset of quenching, on one hand, and the formation of through-wall cracks, cooling behaviour, and hydrogen absorption, on the other hand. No, or only a few, axial cracks were produced during flooding of specimens with oxide scales below approx. 200 μm (see Fig. 7). Thicker oxide scales at the initiation of the quenching phase resulted in a network of through-wall cracks with a density of 0.5-1 mm/mm². The metal surfaces of these cracks were oxidized during cooling from starting temperatures lower than 1673 K, leading to some additional hydrogen production. Most of this hydrogen produced in the cracks was absorbed by the remaining metal phase. Assuming the same crack density in the QUENCH bundle experiments shows that the oxidation of cracks would lead to an additional hydrogen production of only approx. 1 g, i.e. 0.5-8 % of the total H_2 , during the quenching phase for the whole bundle. Nevertheless, the exothermic absorption, i.e. 139 kJ/mol (H_2), is nearly one half of the energy release due to the production of 1 mole H_2 by the Zr oxidation and may act as a local trigger mechanism for further temperature escalations.

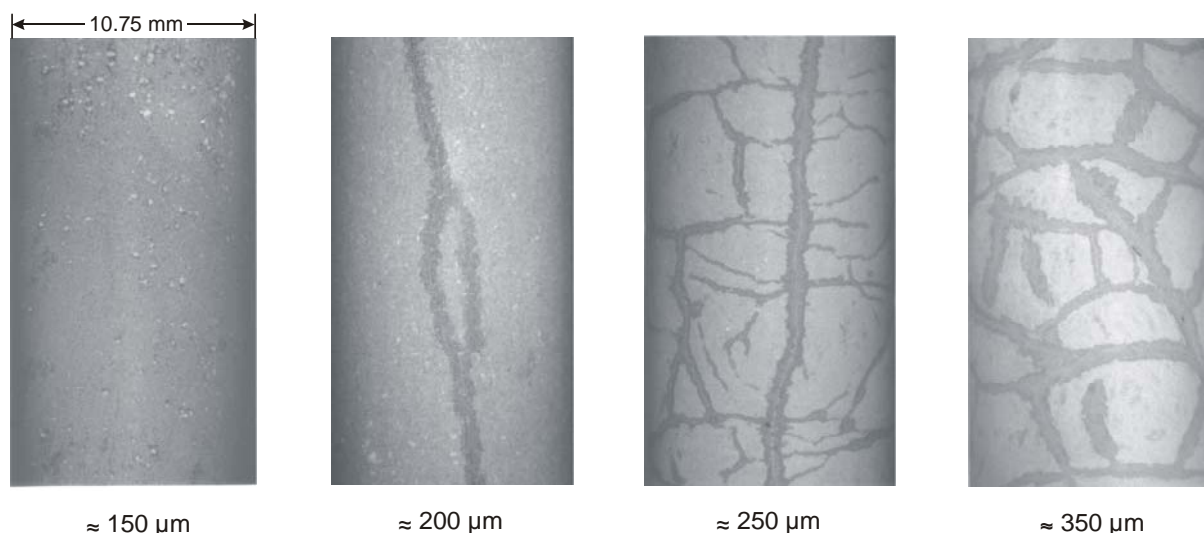


Figure 7: Crack formation in Zircaloy cladding tubes after rapid cooling by steam from 1473 K as a function of cladding pre-oxidation, i.e. initial ZrO_2 layer thickness

Steam starvation

Steam starvation is effective when the steam produced at the bottom of the reactor core is completely consumed from a certain axial elevation upwards, so that the conditions for the upper part of the bundle change from oxidising to reducing ones.

It is conjectured that the 11-min period of steam starvation with temperatures of ~ 2000 K preceding the flooding phase in the bundle test QU-09 is mainly responsible for the large H_2 release by causing a degradation of the protective ZrO_2 scale so that the upper (hotter) regions of the bundle became particularly susceptible to oxygen uptake and an enhanced zirconium oxidation when the high steam flow of 50 g/s was supplied to the test bundle.

To better understand the oxide scale degradation process, special experiments with closed Zircaloy-4 cladding tubes have been conducted in the inductive furnace QUENCH-SR and in the BOX rig. The cladding tube samples were pre-oxidized in an argon-steam flow at ~ 1673 K for 250-2000 s. They were cooled after pre-oxidation and used as reference samples. The other samples were pre-oxidized and afterwards annealed at ~ 1700 K for 600-10800 s under inert conditions. With help of the metallographic examination, both types of samples are compared: the reference sample in the left picture of Fig. 8 with the one which was pre-oxidized in an argon-steam atmosphere and afterwards annealed for three hours in an argon atmosphere (Fig. 8, right picture). The appearance of the reference sample is typical for a Zircaloy cladding when oxygen is supplied from the outside. The sequence of the layers from outside to inside is: ZrO_2 , $\alpha\text{-Zr(O)}$, and $\beta\text{-Zr}$ layer. In the picture on the right hand side one can see a redistribution of the oxygen. The $\beta\text{-Zr}$ phase turned into $\alpha\text{-Zr(O)}$ and the ZrO_2 scale decreased in thickness. Thinner oxide scales were even completely dissolved during the starvation phase in these experiments.

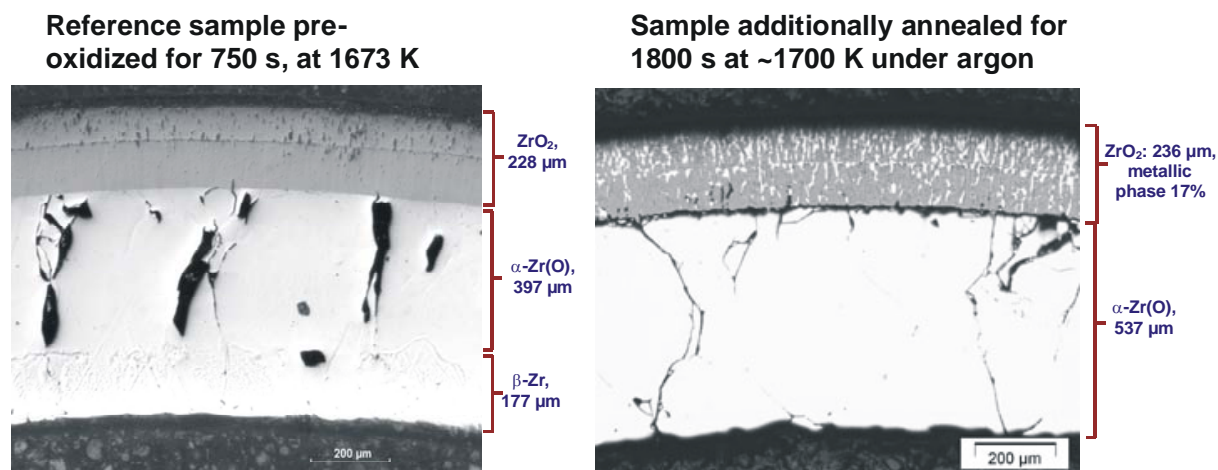


Figure 8: Comparison of an oxidized sample (left) and a sample oxidized and afterwards annealed in an inert atmosphere (right). The relocation of oxygen results in metallic precipitates in the ceramic phase.

B₄C control rod behaviour

This topic was already presented at the Conference on Nuclear Energy for New Europe in 2003 [1]. The oxidation kinetics of various types of boron carbides (pellets, powder) as well as the degradation of B₄C control rod segments were investigated in the temperature range between 800 and 1600 °C. Mass spectrometric gas analysis was used to determine oxidation rates in transient and isothermal tests.

The oxidation kinetics of boron carbide are determined by the formation of a liquid boron oxide layer and its loss due to the reaction with surplus steam to form volatile boric acids and by direct evaporation at temperatures above 1500 °C. Under these test conditions linear oxidation kinetics are established soon after oxidation has initiated. The oxidation kinetics are strongly influenced by the thermal-hydraulic boundary conditions, in particular by the steam flow rate. Only very low amounts of methane were ever produced in these tests.

Enhanced degradation of B₄C control rods starts with the rapid formation of eutectic melts in the systems B₄C-stainless steel (SS) and SS-Zircaloy at temperatures above 1250 °C. Initially, this melt is kept within a ZrO₂ scale formed externally at the Zircaloy guide tube. The absorber melt is rapidly oxidized after failure of the oxide shell and aggressively attacks adjacent fuel claddings.

Almost no methane, which is of interest due to its potential influence on fission product chemistry, was produced during these experiments at high temperatures.

A new result obtained after the last year's conference should finally be presented here. In the SETs with control rod segments, the stainless steel cladding was completely liquefied in all tests above 1500 K. Further tests have been performed to investigate how much steel can be liquefied by B₄C at temperatures 200 K below its melting temperature. Figure 9 shows the results of three tests with 4, 1, and 0.3 wt.% boron carbide in the centre of a steel cylinder. The specimens were kept at 1500 K for 1 hour. The stainless steel samples were completely and homogeneously liquefied by 4 and 1 wt.% boron carbide. The black regions in the macro cross sections of the specimens (Fig. 9) are pores formed during cooldown.

Detailed results on this topic can be found in two recent FZK reports available via the QUENCH web site.

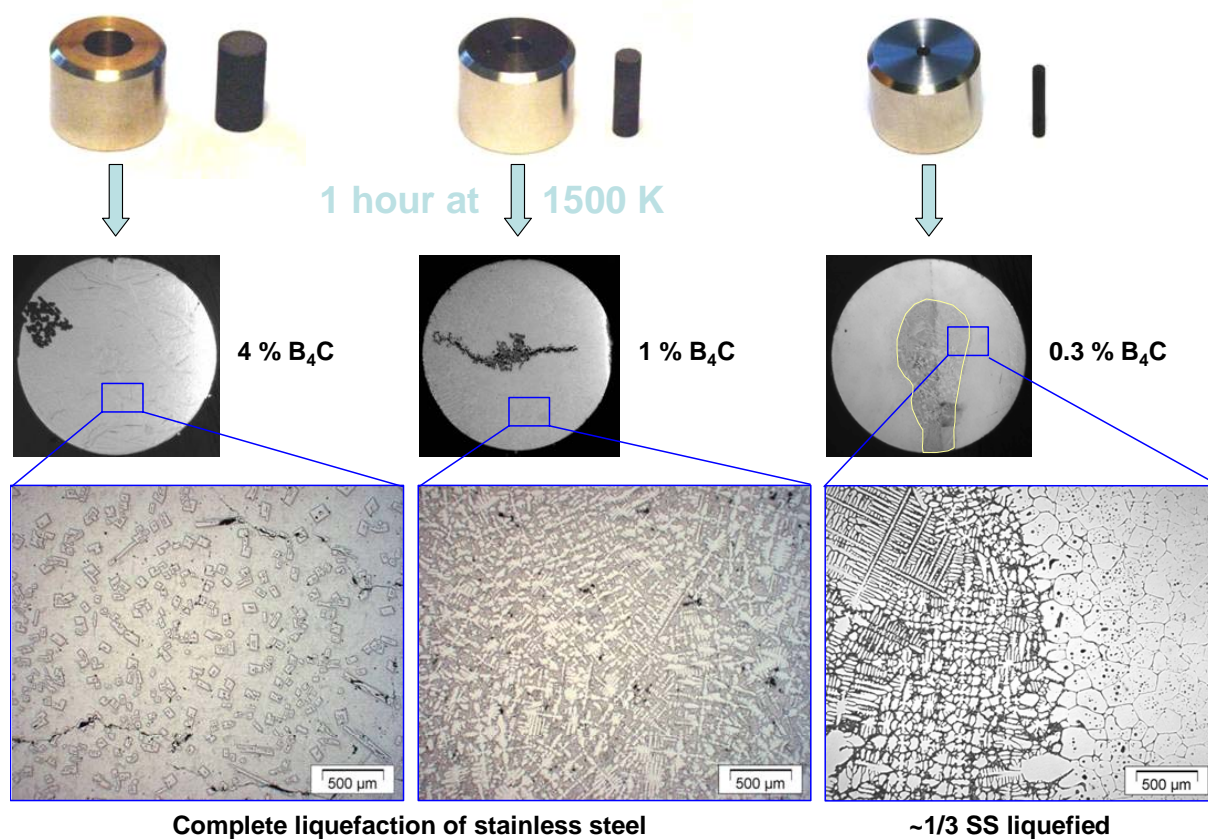


Figure 9: Liquefaction of stainless steel by boron carbide at 1500 K

ACKNOWLEDGMENTS

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- [1] M. Steinbrück, " B₄C Control Rod Behavior during Severe Accident Sequences", Proc. Int. Conf. Nuclear Energy in New Europe 2003, Portorož, Slovenia, September 8-11, Nuclear Society of Slovenia, 2003, CD-ROM, paper No.302.

A complete list of recent reports related to the QUENCH programme can be found at the web site www.fzk.de/quench.