ACCIDENT-TOLERANT FUEL (ATF) CLADDINGS FOR LWRs

ATF materials became worldwide a hot research topic after the Fukushima Daiichi accidents. Karlsruhe Institute of Technology (KIT) is involved in various activities on the development and especially high-temperature characterization of ATF cladding materials. Most of these activities are embedded in international collaborations in the framework of IAEA, OECD-NEA, EU as well as cooperation with partners from industry. With the bundle experiment QUENCH-19, the worldwide first large-scale test of ATF cladding under severe accident conditions was conducted in 2018. This test involved FeCrAl cladding produced and supplied by ORNL. Approx. 100 times less hydrogen was released compared to reference test QUENCH-15 with ZIRLO cladding tubes until the end of the reference test scenario, and a coping time of at least 2000 seconds was confirmed. MAX phase coatings for Zr alloys based on the systems Ti/Cr/Zr + Al + C were produced using a unique two-step procedure based on magnetron sputtered elementary nano-layers and subsequent annealing procedure. Most promising results were obtained with Cr_2AlC coating. High-temperature oxidation tests in steam atmosphere with these MAX phase coatings as well as a number of most promising ATF cladding types including various other coated Zr alloys, FeCrAl, and SiC_f-SiC composites were conducted. Some interesting results with illustrative examples will be presented in this paper.

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INTRODUCTION

Although the nuclear industry has continuously improved the properties and reliability of fuel assemblies (FA) for light water reactors (LWR) since its existence, the fuel rods always were based on UO_2 fuel and zirconium alloy cladding. This materials system works well under operation condition and has resulted into less and less failure rates. The advanced zirconium alloys (Zry) like M5® from Framatome and ZIRLO™ from Westinghouse provide excellent corrosion resistance and mechanical behavior at operation conditions. However, during accident scenarios with high temperatures, strong oxidation in steam-containing atmospheres leads to degradation of the mechanical properties of the cladding tubes as well as production of heat and hydrogen. At temperatures beyond 1200°C the chemical heat release due to the exothermic zirconium-steam reaction may exceed the residual decay heat and thus strongly affect the accident progression. The released hydrogen bears the risk of hydrogen detonations when coming in contact with oxygen/air.

Latest since the Fukushima Daiichi accidents the nuclear community started thinking about alternatives to the UO_2/Zry system with one main focus on reducing heat and hydrogen release during severe accident scenarios, and thus increasing coping time for accident management measures (AMM), while retaining or even improving the fuel assembly properties during normal operation. Further issues include of course reasonable costs, licensing as well as front end and back end performance.

Today, the development of accident tolerant fuel (ATF), advanced cladding and other structure material is pushed by industry and research organizations worldwide mainly in the US, Asia and Europe. Furthermore, ATF research is coordinated by international organizations like the IAEA, OECD-NEA and the European Commission. So, recently, NEA published an extensive (>300 pages) state-of-the-art report on ATF prepared by an international expert group (EGATFL) including scenarios and metrics, cladding, fuel, and technology readiness level evaluation [1]. An excellent overview paper on ATF cladding development (in the opinion of the author) with many references was published by Terrani in 2018 [2].

MATERIALS SELECTION FOR ATF CLADDINGS

Zirconia (ZrO_2) formed during oxidation of zirconium alloys is a very stable and well adherent oxide, but

VAINAS DE COMBUSTIBLE TOLERANTE A ACCIDENTES (ATF) PARA LWR

Los materiales ATF se han convertido en un tema de investigación mundial tras los accidentes de Fukushima Daiichi. El Instituto de Tecnología de Karlsruhe (KIT) está involucrado en diversas actividades relacionadas con el desarrollo y especialmente en la caracterización a alta temperatura de los materiales de vaina tipo ATF. La mayoría de estas actividades están integradas en colaboraciones internacionales en el marco del OIEA, OCDE-NEA, UE, así como la cooperación con la industria nuclear. En cuanto a las actividades realizadas por el KIT cabe destacar que en 2018 se realizó el experimento QUENCH-19, que es la primera prueba a gran escala de vainas ATF en condiciones de accidentes graves. Esta prueba se realizó con el material de vaina FeCrAl fabricado y suministrado por ORNL. Durante dicho experimento se liberó una cantidad 100 veces menor de hidrógeno en comparación con el experimento de referencia QUENCH-15 con vainas Zirlo, y se confirmó un tiempo disponible hasta fallo de al menos 2000 segundos. Los recubrimientos de fase MAX para aleaciones de Zr basados en los sistemas Ti/Cr/Zr + Al + C se obtuvieron utilizando un procedimiento único de dos pasos basado en nano capas primarias pulverizadas mediante un magnetrón y con un procedimiento posterior de recocido. Los resultados más prometedores se obtuvieron con el recubrimiento Cr_2AlC. Se llevaron a cabo pruebas de oxidación a alta temperatura en atmósfera de vapor con estos revestimientos de fase MAX, así como una serie de los tipos de revestimiento de ATF más prometedores, incluidos otros compuestos Zr aleados, FeCrAl y SiC_f-SiC. En este artículo se presentan algunos ejemplos ilustrativos con resultados interesantes.

it is characterized by high oxygen diffusion and thus does not effectively protect the underlying metal at high temperatures. High-temperature oxidation resistance of materials generally relies on the formation of stable oxides which act as diffusion barriers, namely chromia (Cr_2O_3), alumina (Al_2O_3), and silica (SiO_2) (Figure 1). The three most promising ATF cladding technologies worldwide under development, i.e. (1) coated Zr-based cladding, (2) iron-chromium-aluminum (FeCrAl) alloys, and (3) SiC_f-SiC ceramic-matrix composites (CMC) consist of materials forming one of these oxides during oxidation at high temperatures. The most near-term solution seems to be high-temperature oxidation resistant coatings on Zr alloys [3].

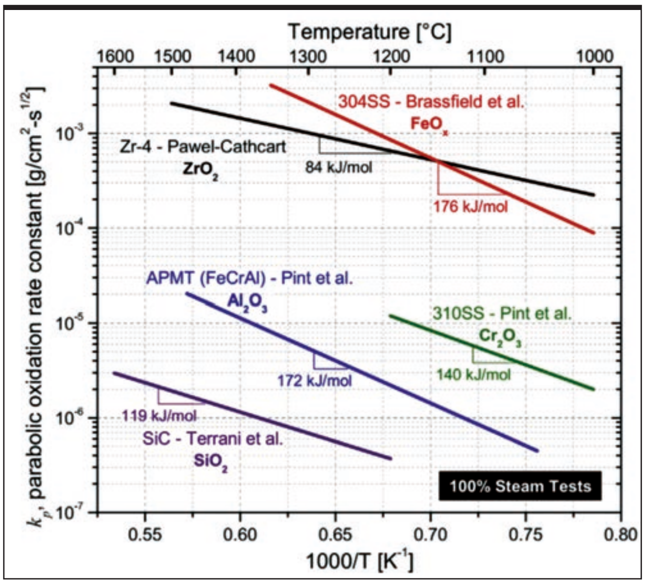


Figure 1. Oxidation kinetics of potential ATF cladding materials forming Cr_2O_3, Al_2O_3, and SiO_2, respectively. The graph shows 2-4 orders of magnitude lower oxidation rates compared to zirconium alloys and classical reactor steel (from [2]).

Among these coatings, chromium (Cr) and chromium-based alloys are worldwide most widely explored. In addition to the relatively simple manufacturing of Cr-coated cladding tubes and their excellent high-temperature oxidation resistance up to ca. 1300°C, the superficial chromia layer formed during oxidation is the only oxide of the three, mentioned above, which is stable under LWR operation conditions. Al_2O_3 and SiO_2 may suffer so-called hydrothermal corrosion at the conditions of high temperature and pressure in LWRs, i.e. they are dissolved in water [3]. For that reason, other, more complex compounds are under development forming chromia at lower temperatures (during operation) and alumina at high temperatures under accident conditions. Such compounds are for instance MAX phases like Cr_2AlC which combine favorable properties of metals and ceramics at the same time [4] [5]. Many more metal or ceramic coating types are under investigation worldwide [3]. The main advantage of coated Zry cladding solutions is that they are rather compatible with existing zirconium technologies and licensing procedures. At the same time, this still Zr-based solution may be also the biggest drawback in case of coating failure at very high temperatures under accident conditions.

FeCrAl alloys are another potential candidate for ATF cladding because they also form chromia at lower temperatures (during operation) and alumina at high temperatures under accident conditions [6]. They are cheap and easy to produce and show very good corrosion and high-temperature oxidation resistance. The main issues with FeCrAl alloys are the neutronic penalty, relatively low melting temperature and potential tritium permeability.

Silicon carbide (SiC) based ceramic fiber-matrix composites offer the best high-temperature behavior of all ATF cladding candidates up to at least 1700°C [7]. This first of a kind ceramic solution for cladding tubes is a rather long-term development. In addition to the excellent high-temperature oxidation resistance, SiC provides a very good neutronic behavior. In-pile hydrothermal corrosion and leak tightness issues seem to be the biggest drawbacks.

Obviously, there is no ideal solution for new accident-tolerant fuel cladding. Therefore, many research efforts on ATF cladding and also accident tolerant fuels and other structure components [1], not discussed in this paper, are internationally going on. The QUENCH group at Karlsruhe Institute of Technology (KIT) is one of the worldwide leading laboratories working on high-temperature characterization of materials under prototypic atmospheres. The QUENCH bundle facility is a unique large-scale out-of-pile facility for the integral investigation of hydrogen source term and materials interactions during the early phase of severe accidents [8]. Smaller-scale lab experiments in high-temperature furnaces and thermo-gravimetric devices are applied for separate-effects investigations. The QUENCH group is involved in a number of international collaborations in the framework of IAEA, OECD-NEA and EC as well in the Westinghouse led CARAT program. In this paper, a number of interesting examples, from the author's point of view, obtained at KIT on the high-temperature behavior of ATF cladding candidates are presented and briefly discussed.

ATF RELATED RESEARCH AT KIT

In this chapter, examples will be given on development and qualification of ATF cladding taking into account the three most promising concepts mentioned above. Much more work has been done at KIT especially on high-temperature oxidation in round robin exercises in the framework of international collaborations.

Bundle test QUENCH-19 with FeCrAl cladding

The worldwide first large-scale bundle test with ATF cladding material, namely with the FeCrAl alloy B136Y3 (Century Tubes Inc. /ORNL), was conducted in the QUENCH facility in cooperation with ORNL, USA, in August 2018 [9]. This facility is a large-scale bundle facility with 24 electrically heated, >2 m long fuel rod simulators [8]. It is extensively instrumented with high-temperature thermocouples, pressure gauges, level meters, etc. and coupled with a mass spectrometer for analysis of hydrogen and other gases. Usually, experiments are completed by reflooding (which gave the facility the name). The QUENCH-19 experiment with FeCrAl cladding was run with a very similar scenario than test QUENCH-15 with ZIRLO (Zr1Nb1Sn alloy) cladding with respect to bundle geometry and power input as could be seen in Figure 2. The FeCrAl experiment was run 2000 s longer at the highest power input until first local melting of the FeCrAl cladding was expected. Hence, the FeCrAl bundle was quenched 2000 s later than the ZIRLO bundle.

As expected, the hydrogen release was much less in the FeCrAl

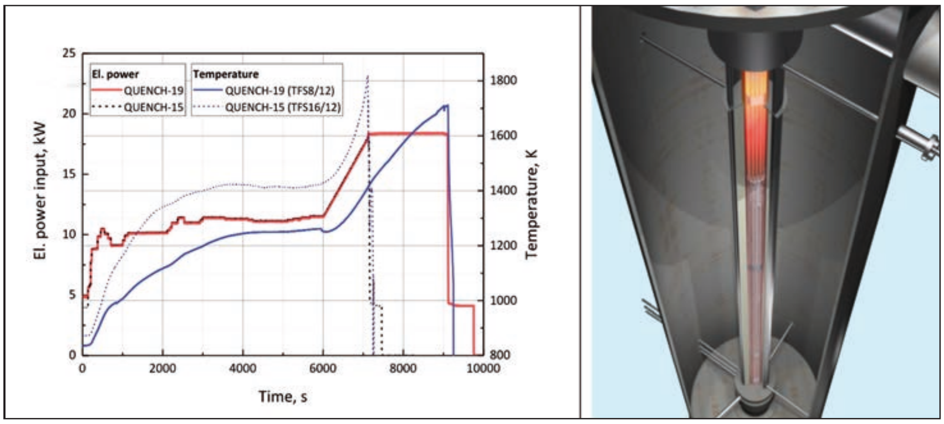


Figure 2. Left: Electric power input and bundle temperature in the hot zone for QUENCH-19 (FeCrAl) and reference test QUENCH-15 (ZIRLO); right: Scheme of the QUENCH facility during the reflood phase.

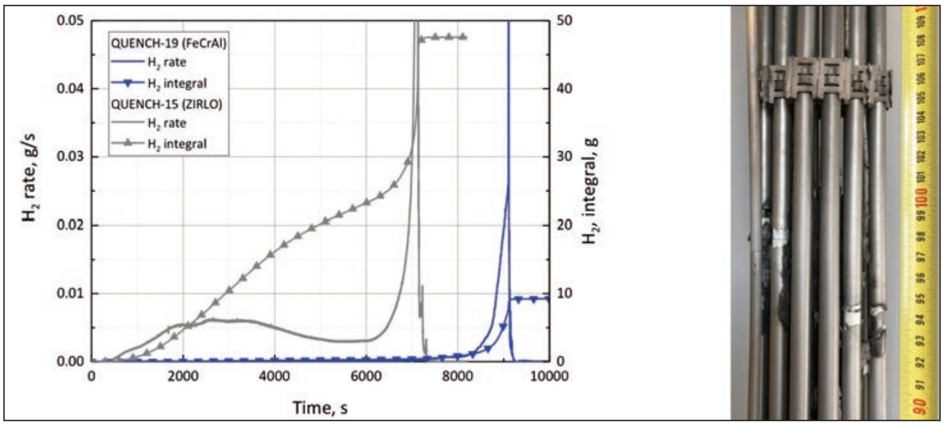


Figure 3. Left: Hydrogen release during experiment QUENCH-19 (FeCrAl) and reference test QUENCH-15 (ZIRLO); Right: Post-test appearance of the QUENCH-19 bundle.

experiment: Until the time when the QUENCH-15 test was terminated by reflood, 100x less hydrogen was produced in the QUENCH-19 experiments (0.4 g and 40 g, respectively) (Figure 3). Even at the end of the QUENCH-19 test after 2000 s more heating at the highest power level, only 9 g hydrogen was measured compared to about 47 g in the shorter test with ZIRLO.

Some melt formation was seen in the bundle after the test which mainly came from stainless steel (SS 304) thermocouple sheaths. Rupture of some cladding tubes was observed most probably caused by strong shrinking during the quench phase due to the two times higher thermal expansion coefficient of FeCrAl compared to Zr alloys. Only low oxidation of the FeCrAl surfaces unaffected by SS melt attack was seen along the whole bundle. The bundle was embedded in epoxy resin and will be cut into slices for more detailed metallographic post-test examination.

The bundle test was accompanied by small-scale furnace tests on the high-temperature oxidation of FeCrAl alloys in dependence on alloy composition and heating schedule [10]. This study showed that the formation of a protective alumina scale at elevated temperatures is not only dependent on the (high enough) concentration of chromium and aluminum in the alloy, but also considerably influenced by the heating rate. Too fast heating may impede diffusion of enough aluminum to the surface for building up the protective scale and finally result in rapid, so-called catastrophic oxidation. More experiments on the oxidation kinetics of various commercial and research FeCrAl alloys are ongoing at KIT.

Development of MAX phase coatings

MAX phases are a family of layered, hexagonal carbides or nitrides with the general formula $M_{n+1}AX_n$ (n=1-3) where M is an early transition metal, A is an A-group element and X is either carbon or nitrogen. These compounds possess a special combination of chemical, physical, electrical, and mechanical properties having both metallic and ceramic characteristics. Some MAX phases are known to be very resistant against high-temperature oxidation in air and steam. This was the reason to investigate MAX phas-

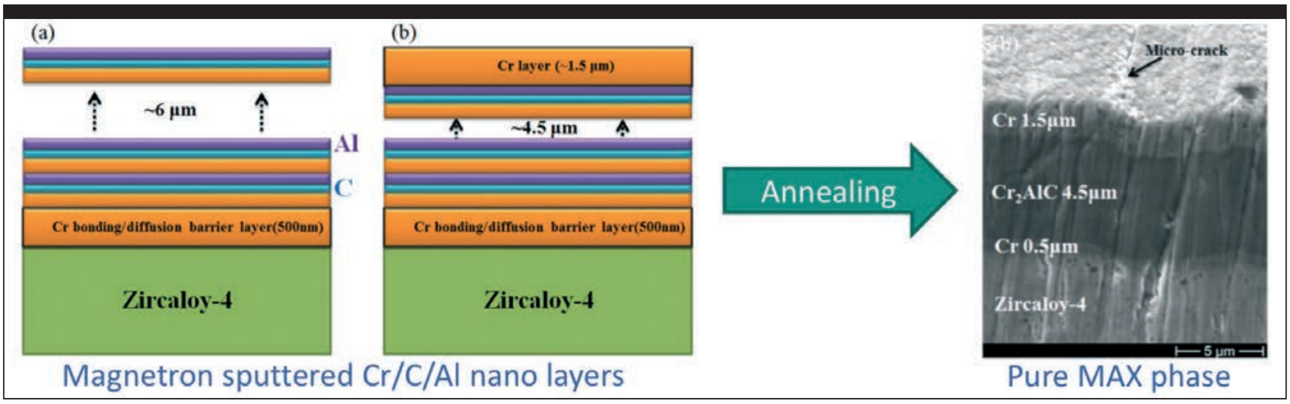


Figura 4. Synthesis of phase-pure Cr2AlC MAX phase coating on Zircaloy-4 substrate: 1) Magnetron sputtering with three element targets of nanoscale multilayer stacks and 2) subsequent annealing at 500°C in inert atmosphere.

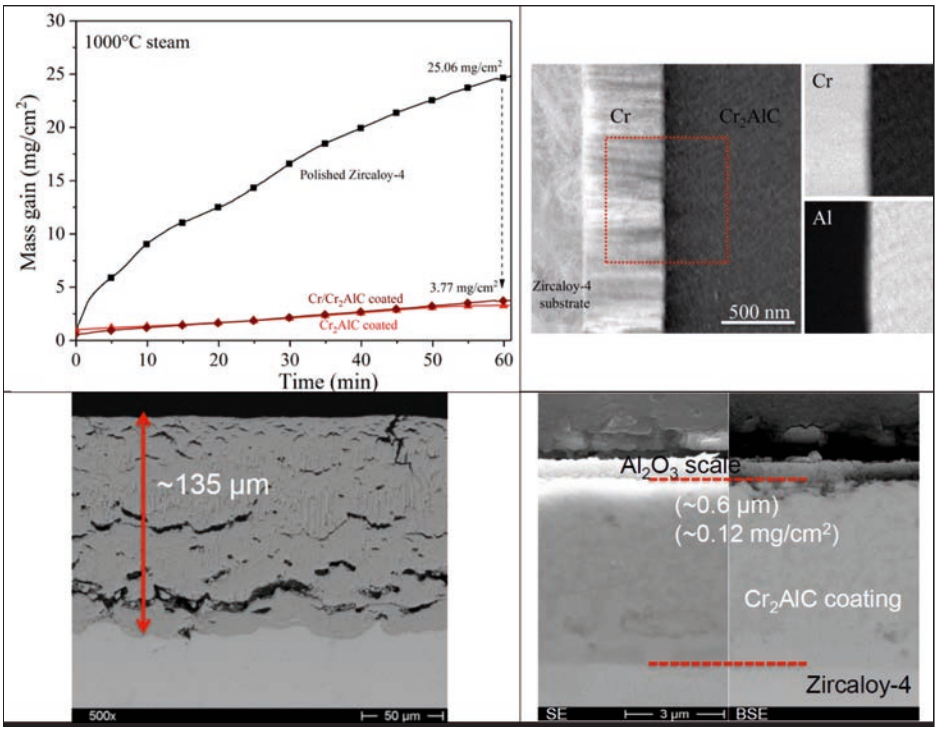


Figura 5. One hour oxidation of Cr_2AlC on Zry-4 at 1000°C in steam; Top, left: TG curves of two coating design compared to non-coated Zry-4; Top, right: STEM image of Cr_2AlC/Cr interface and corresponding EDS mapping before oxidation; Bottom, left: SEM image of non-coated Zry-4 reference sample, Bottom, right: SEM image of coated sample after oxidation.

es as oxidation resistant coatings on zirconium alloys in the framework of a PhD work [11].

Ti_2AlC, Cr_2AlC and Zr_2AlC on Zircaloy-4 substrates were tested with the best results obtained for the Cr-containing MAX phase with respect to coating properties and oxidation resistance. The coatings were synthesized by a two-step process consisting of magnetron sputtering of nanoscale elemental multilayer stacks and subsequent thermal annealing (Figure 4). Different coating designs were tested including chromium bonding and diffusion barrier to suppress aluminum diffusion into the substrate and chromium top layer for protection against hydrothermal corrosion as explained above.

The coated samples were tested in autoclave tests at Westinghouse labs in the U.S. as well as for high-temperature oxidation in steam. 3 days autoclave tests at 360°C and 18.8 MPa resulted in partial delamination of the coatings. But generally the Cr_2AlC coatings showed an excellent corrosion resistance with the formation of an ultrathin oxide layer undetectable by standard scanning electron microscopy (SEM). Furthermore, no diffusion of elements between coating and bulk was observed. In the future, adjusting deposition and heat treatment parameters are planned to avoid delamination and cracking as well as to relief stresses.

High-temperature oxidation tests in steam exhibited very promising results of the Cr_2AlC coated samples. Figure 5 provides as an example results after one hour oxidation tests at 1000°C in steam. The mass gain of the coated samples was significantly reduced by the protective coating. This was also reflected by the metallographic post-test analysis showing a much thinner aluminum oxide scale on the MAX phase coating compared to zirconium oxide formed on the non-coated Zircaloy-4. In addition, a scanning transmission electron microscopy (STEM) with corresponding element mappings for Cr and Al is given in the figure showing the perfect adherence and phase purity of the coating layers after annealing.

Ultra-high temperature oxidation tests with SiCf-SiC ceramic composite cladding tube segments

First experiments up to 2000°C were already conducted a few years ago with SiC_f-SiC samples from CTP (Ceramic Tubular Products, Llc.) partly surviving oxidation in steam and quenching with water from such high temperatures [12]. More recently, two SiC_f-SiC tube segments from General Atomics were investigated in collaboration with Westinghouse. The results of these experiments should be briefly discussed here.

The 5-cm long tube segments were filled with graphite as susceptor for the inductive heating and leak tightly closed with SiC plugs at both ends by welding with SiC precursor polymer. Figure 6 shows three images of such a sample. The longitudinal cut through a neutron tomography image provides information about the

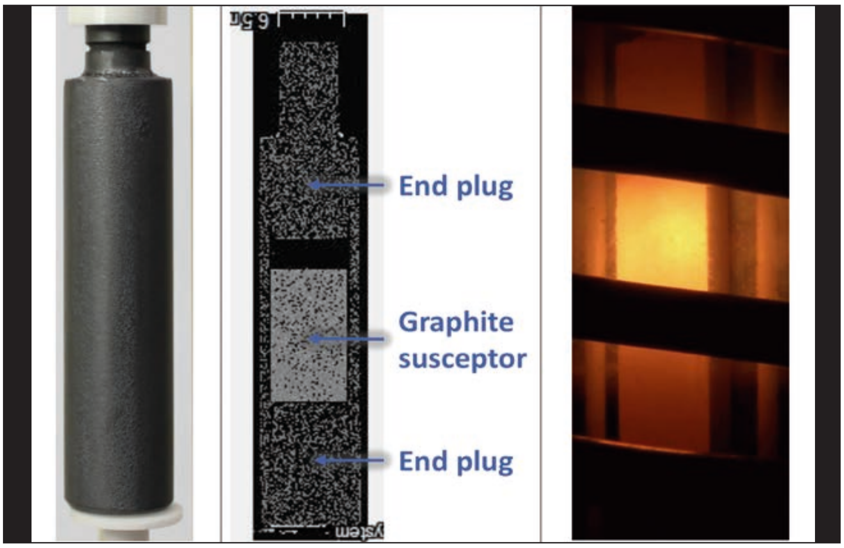


Figura 6. SiC_f-SiC sample as received and installed in the sample holder (left), neutron tomography image (mid), and during experiment in the QUENCH-SR rig (right).

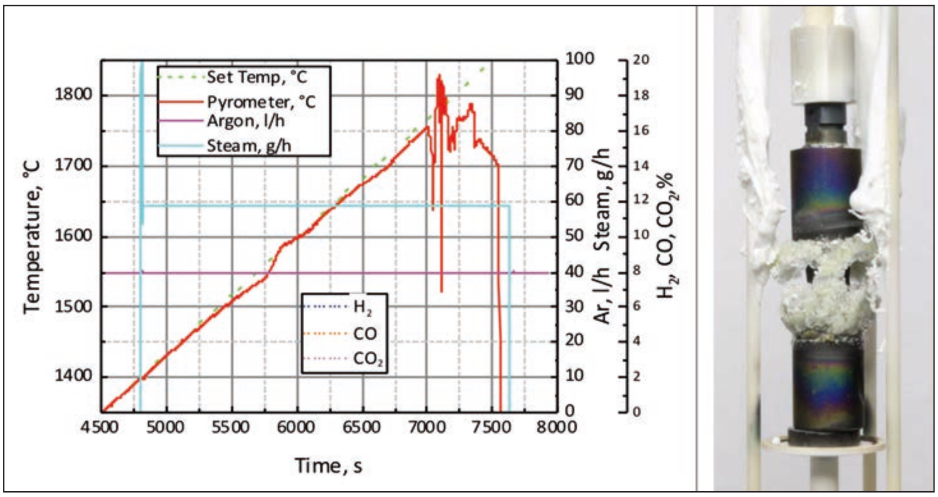


Figura 7. Conduct and results of the transient experiment with SiCf-SiC. Left: Temperature, gas/steam injection, and MS results for hydrogen, CO and CO$_2$; Right: Post-test appearance of the sample.

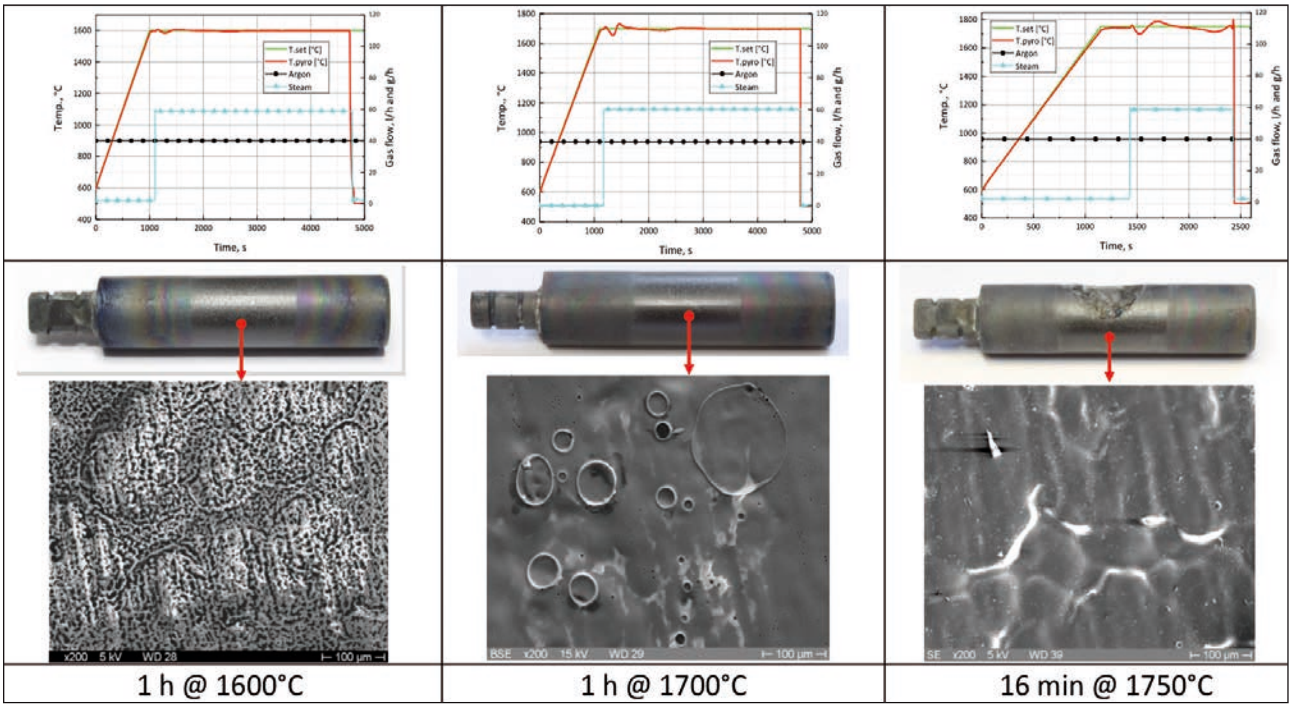
dimensions of the graphite core and the end plugs. The right image shows the sample in the facility at approx. 1600°C with a strong axial temperature gradient caused by the limited dimensions of the graphite susceptor.

The tests were conducted in the QUENCH-SR (single rod) facility with inductive heating, coupled with a CEM (controlled evaporator and mixing) unit for oxidation tests in well-defined steam atmosphere at the inlet and a mass spectrometer (MS) for off-gas analysis at the outlet [13]. Final quenching is possible by a rising cylinder filled with water. A transient test from 1400 to 1800°C was conducted with one sample and three subsequent isothermal tests at 1600, 1700, and 1750°C were done with the second sample.

The transient test went smooth with respect to heating schedule and only limited gaseous reaction products measured by MS until approx. 1750°C. At further rising temperatures, bubble formation (of liquid silica scale at this temperature), volatilization of the SiO_x and strong increase in production of H_2, CO, and CO_2 was observed as could be seen in Figure 7. The temperature signal became very unstable because the pyrometer, used to measure and control temperatures, was disturbed by the formed smoke and changing surface of the sample. Finally the test had to be stopped at nominally 1850°C. The SiC_f-SiC was completely consumed in the hot central part of the tube segment, and precipitated SiO_x was seen at colder parts of the sample holder (Figure 7 (right)). More detailed post-test examinations of this sample revealed a ca. 4 µm thick silica layer on the remaining part of the CMC cladding, intact welds between tube and end plugs as well as no chemical interactions between the graphite susceptor and SiC tube.

The second sample was used for three subsequently conducted isothermal tests at nominally 1600, 1700, and 1750°C with the conditions shown in Figure 8. All tests should be terminated by quenching with water. Due to technical issues, the first test at 1600°C was finished by fast cooldown in steam, the test at 1700°C by quenching in hot water, and the test at 1750°C by quenching in cool water. No special effect of quenching was seen.

Generally, the tests at 1600°C and 1700°C resulted in only low gas release during the steam oxidation. The samples remained completely



1 h @ 1600°C

1 h @ 1700°C

16 min @ 1750°C

Figura 8. Test conduct and post-test appearance (macrographs and SEM images) SiC sample after isothermal tests.

intact with only slight changes of the surface appearance due to the formation of thin silica scales. Figur 8 provides post-test images of the sample and typical SEM images of the sample surface in the hot zone. EDX analyses confirmed the formation of a superficial protective oxide scale. Typical remnants of SiO_2 bubbles were seen after the test at 1700°C.

The test at 1750°C had to be terminated earlier as planned due to local degradation connected with significant release of gases and white smoke. The gas release rates increased by more than two orders of magnitude after approx. 15 min oxidation in steam. Bubble formation was already seen before failure. Fig. 8 shows the sample with failure position and a surface SEM image of near the failure position. The sample was also embedded after the final test at 1750°C and longitudinally cut for post-test analysis by optical microscopy. The local failure occurred by loss of the protective CVD layer and corresponding attack of the carbon covered fibers. The graphite core was not attacked at all by steam or interaction with SiC. Similar to sample of the transient test, a rather abrupt transition from well preserved to completely consumed CVD protective layer was observed. No oxide scale was visible with the resolution of the optical microscope although SiO_x (and C) was detected at the surface of the sample by EDX.

One can conclude from the high-temperature oxidation tests with silicon carbide cladding conducted so far, that they possess excellent resistance against oxidation in steam atmosphere up to 1700°C as a result of the formation of a protective silica scale under these conditions. Furthermore, the samples survived quenching in water from 1700°C and 1750°C without any signs of thermo-mechanical failure.

The SiC consumption rates at 1600°C and 1700°C, as well as at 1750°C before failure, were in the order of 0.01 g/m^2s resulting in approx. 10 µm/h corrosion rate. Given an approx. 300 µm thick protective CVD layer covering the fiber-matrix composite material, such cladding tubes could survive more than a day at such extreme conditions.

SUMMARY AND OUTLOOK

ATF cladding materials should improve oxidation resistance during severe accidents, i.e. high-temperatures, and hence reduce the risk of mechanical degradation and extensive hydrogen release which caused the detonations during the Fukushima-Daiichi accidents. Worldwide, serious activities are progressing on the development of ATF cladding tubes. The most promising concepts today for near-term are coated Zry tubes and FeCrAl alloys and for long-term silicon carbide CMCs. Maximum tolerable temperatures without severe hydrogen production are around 1300, 1400, and 1700°C, respectively.

At KIT, more experiments are foreseen in the QUENCH-SR rig with different ATF cladding candidates, with coated Zr alloys and SiC in the framework of collaboration with various manufacturers. Furthermore, a Joint Undertaking coordinated by the OECD-NEA is currently under discussion with participants mainly from the US and Europe, which should include three bundle QUENCH tests with different ATF cladding tubes and accident scenarios.

ACKNOWLEDGEMENTS

The work presented in this paper was performed by the QUENCH team at the Institute for Applied Materials (IAM-AWP) at KIT in the framework of the nuclear safety program NUSAFE. Special thanks go to J. Stuckert, J. Moch, M. Große, C. Tang, and U. Stegmaier as well as to M. Stueber from the coating group of the institute. The bundle test QUENCH-19 was conducted in cooperation with Oakridge National Laboratories, TN, USA with strong support from K. Terrani.

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Steinbrück, M.
Accident-tolerant fuel (ATF) claddings for LWRs.
2019. Nuclear España, 411.
doi: 10.5445/IR/1000127772

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Accident-tolerant fuel (ATF) claddings for LWRs.
2019. Nuclear España, 411, 32–37.